

PATENT ABSTRACTS OF JAPAN

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(54) POLYIMIDE FILM AND ITS PRODUCTION

(57)Abstract:

PROBLEM TO BE SOLVED: To provide an excellent polyimide film having high modulus of elasticity, high storage elastic modulus, high extensibility, low coefficient of linear expansion comparable to that of a copper foil, and low coefficient of expansion on absorption of moisture.

SOLUTION: The polyimide film is produced from a polyamic acid obtained by reacting p-phenylenebis(trimellitic acid monoester anhydride), oxydiphthalic acid dianhydride, p-phenylenediamine, 4,4'-diaminodiphenyl ether and at least one acid dianhydride selected from the group consisting of pyromellitic dianhydride, 3,3',4,4'-benzophenonetetracarboxylic dianhydride and 3,3',4,4'-biphenyltetracarboxylic dianhydride in an organic solvent.

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CLAIMS

[Claim(s)]

[Claim 1] p-phenylene screw (trimellitic acid monoester anhydride) and oxy-JIFUTARU acid 2 anhydride, P-phenylene diamine and 4 and 4'-diamino diphenyl ether, and (pyromellitic acid 2 anhydride, 3, 3', 4, and 4' - benzophenone tetracarboxylic dianhydride —) The polyimide film characterized by being manufactured from the polyamide acid which five sorts of monomers which consist of one chosen from 3, 3', and 4 and the group which consists of 4'-biphenyl tetracarboxylic dianhydride are made to react in an organic solvent, and is obtained.

[Claim 2] In the polyimide film manufactured from said polyamide acid the addition of said monomer p-phenylene screw (trimellitic acid monoester anhydride) is 1-90-mol % to all acid 2 anhydride. Oxy-JIFUTARU acid 2 anhydride is 8-85-mol % to all acid 2 anhydride. pyromellitic acid 2 anhydride, 3, 3', 4, and 4' - benzophenone tetracarboxylic dianhydride — One chosen from 3, 3', and 4 and the group which consists of 4'-biphenyl tetracarboxylic dianhydride It is 2-14-mol % to all acid 2 anhydride. P-phenylene diamine The polyimide film according to claim 1 which is 25-90-mol % and is characterized by 4 and 4'-diamino diphenyl ether being 10-75-mol % to all diamines to all diamines.

[Claim 3] The polyimide film characterized by being the polyimide film indicated by claim 1 or claim 2, and a storage modulus [in / elongation percentage / modulus of elasticity in tension / 15-30 ppm and / mean coefficient of linear expansion / 100 degrees-C or more / mean coefficient of linear expansion 200 degrees C or less / a moisture absorption expansion coefficient 20% or more, and / in Tg / 200 degrees C or more, and 300 degrees-C or more temperature of 400 degrees C or less] being 200 or more MPas at the time of 4.5 - 8.5GPa and fracture. [10 ppm or less]

[Claim 4] 4 and 4'-diamino diphenyl ether is dissolved into an organic solvent. pyromellitic acid 2 anhydride, 3, 3', 4, and 4' - benzophenone tetracarboxylic dianhydride — One chosen from 3, 3', and 4 and the group which consists of 4'-biphenyl tetracarboxylic dianhydride is added. Then, add p-phenylene diamine and p-phenylene screw (trimellitic acid monoester anhydride) is added to this organic solvent solution. Then, the manufacture approach of the polyimide film which carries out the dehydration ring closure of the polyamide acid polymer which added oxy-JIFUTARU acid 2 anhydride and was obtained using an acid anhydride and a tertiary amine, and is characterized by obtaining a polyimide film.

[Claim 5] p-phenylene diamine is dissolved into an organic solvent — making (pyromellitic acid — 2 anhydride) One chosen from 3, 3', and the group that consists of - benzophenone tetracarboxylic dianhydride, 3, 3', and 4 and 4' 4, 4'-biphenyl tetracarboxylic dianhydride is added. Then, p-phenylene screw (trimellitic acid monoester anhydride) is added, 4 and 4'-diamino diphenyl ether is added to this organic solvent solution. Then, the manufacture approach of the polyimide film which carries out the dehydration ring closure of the polyamide acid polymer which added oxy-JIFUTARU acid 2 anhydride and was obtained using an acid anhydride and a tertiary amine, and is characterized by obtaining a polyimide film.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the polyimide film excellent in the physical-properties balance which can give low curvature and high dimensional stability in a metal, especially a lamination product with copper.

[0002]

[Description of the Prior Art] The polyimide film is equipped with thermal resistance, insulation, solvent resistance, a low temperature performance-proof, etc., and is widely used for the computer list as an electrical-and-electric-equipment components ingredient of IC control.

[0003] In recent years, a computer list is asked for a miniaturization and thin shape-ization also for wiring substrates and an IC package ingredient with a miniaturization and thin-shape-izing of the electrical and electric equipment of IC control. For this reason, it is needed to be heating, to be tension, and that the dimensional change according to moisture absorption further is small also about the polyimide film with which the circuit pattern given to these also becomes minute; and is used for a flexible patchboard, the carrier tape for TAB, etc. Furthermore, it is necessary with thin-shape-izing of an ingredient to maintain the "elasticity" of the whole layered product and to make a processing process stability.

[0004] In order to fulfill such need, it is desired for coefficient of linear expansion of a polyimide film to be small, for an elastic modulus and a storage modulus to be high, and for a moisture absorption expansion coefficient to be low.

[0005] However, in order to make a polyimide film and copper foil rival and to process them in the case of manufacture of a flexible patchboard or an IC package, it is not desirable to differ from a copper coefficient of linear expansion greatly about film coefficient of linear expansion. That is, it is because curvature will arise in a lamination article, and it will be hard coming to carry out processing, consequently overall dimensional accuracy and the overall yield will fall, if the coefficient of linear expansion of a polyimide film and copper foil differs greatly. Therefore, what has the small difference of coefficient of linear expansion with copper foil is desirable.

[0006] Various attempts are made in order to obtain the polyimide film which has the above-mentioned property. First, for rate[of high elasticity]-izing of a polyimide film, it is known widely that what is necessary is just to use the monomer of upright structure, i.e., a monomer with high linearity. The coefficient of linear expansion of the ***** film for large quantities becomes low too much, and stops however, being suitable for the application of lamination with copper foil in a monomer with high linearity.

[0007] Though a comparatively high elastic modulus is realized, in order not to lower coefficient of linear expansion too much, using the monomer which has comparatively upright structure, not using a chemical imide-ized agent, it manufactures by the heat cure method, and there is also an example which takes the approach of making orientation of the direction of a field sweet. However, the heat cure method has the disadvantage that required heating time is long compared with the chemical cure method, and it is inferior to productivity.

[0008] Furthermore, if it is upright and a monomer with high linearity is used, generally, the flexibility of a film is spoiled and difficulty may produce it at the point which is one of the advantages as a flexible patchboard etc. that bending is possible.

[0009] Especially for a semiconductor package application, it is called for from a viewpoint of the dependability of a semi-conductor that water absorption is low as much as possible, and it is called for from a viewpoint of dimensional stability from it that a moisture absorption expansion coefficient is also low.

[0010] In order to lower water absorption and a moisture absorption expansion coefficient, it is effective to reduce the imide radical weight in the molecular structure. For this reason, the long-chain monomer which contains two or more crookedness radicals in a principal chain is used in many cases. However, as a result, decline in an elastic modulus and too much increase of coefficient of linear expansion are caused, and dimensional stability falls victim. When extreme, thermoplasticity which has Tg at low temperature 200 degrees C or less comes to be shown, and it stops being suitable for using as a base film. Moreover, when the long monomer was used with such linearity, packing of a chain could not become difficult, and sufficient toughness could not be discovered, but there were problems, like film-izing depending on the case itself becomes difficult.

[0011] Generally moreover, the value of the storage modulus of a viscoelastic body (a polyimide film is also contained) in the temperature field exceeding Tg, it becomes lower than the value of the storage modulus in ordinary temperature (a single figure). When the storage modulus in the temperature (for example, 300 degrees C or more 400 degrees C or less) which what figures about triple [2-] become low depending on the case is known, and is usually used for film production is extremely small, When a film curtains extremely in the temperature field of film production, it may become difficult to produce a flat film without sag itself.

[0012] As mentioned above, there were many points which should be taken [workability / of a film] into consideration besides these properties in order to realize all of the rate of high elasticity demanded as a property of a polyimide film, a high storage modulus, low coefficient of linear expansion, and the property of low absorptivity, and it was in the especially difficult situation to obtain the polyimide film with which there are problems, like other properties fall victim and it has a polyimide film and two or more good properties of all when it is going to satisfy one of properties.

[0013]

[Problem(s) to be Solved by the Invention] Then, this invention persons solved the above-mentioned trouble, and as a result of examining wholeheartedly manufacturing the polyimide film suitable for the flexible printed circuit board and TAB film of thin wiring

which has many properties of all of the rate of high elasticity, a high storage modulus, the coefficient of linear expansion near copper, sufficient toughness, low water absorption, and a low moisture absorption expansion coefficient, they resulted in this invention.

[0014]

[Means for Solving the Problem] this invention persons found out the polyimide film which can realize and control many property balance to altitude specifically, and its manufacture approach in the polyimide film of a specific presentation in view of the above-mentioned demand.

[0015] The place made into the summary of the polyimide film concerning this invention p-phenylene screw (trimellitic acid monoester anhydride), oxy-JIFUTARU acid 2 anhydride, pyromellitic acid 2 anhydride, 3, 3', 4, and 4' - benzophenone tetracarboxylic dianhydride - It makes into the contents to be manufactured from 3, 3', and the polyamide acid that one chosen from group which consists of - biphenyl tetracarboxylic dianhydride, p-phenylene diamine, and 4 and 4' 4, 4'-diamino diphenyl ether is made to react in an organic solvent, and is obtained.

[0016] In said polyimide film the above-mentioned p-phenylene screw (trimellitic acid monoester anhydride) It is 1-90-mol % to all acid 2 anhydride. Oxy-JIFUTARU acid 2 anhydride all acid 2 anhydride -- receiving -- eight-mol % - 85-mol % -- it is (pyromellitic acid -- 2 anhydride) One chosen from 3, 3', and the group that consists of - benzophenone tetracarboxylic dianhydride, 3, 3', and 4 and 4' 4, 4'-biphenyl tetracarboxylic dianhydride It makes to be %, for p-phenylene diamine to be 25-90-mol % to all diamines, and for 4 and 4'-diamino diphenyl ether to 2-14-mol be 10-75-mol % to all diamines into the contents to all acid 2 anhydride.

[0017] In the polyimide film to apply, it makes for a storage modulus [in / elongation percentage / modulus of elasticity in tension / 15-30 ppm and / mean coefficient of linear expansion / between 100 degrees C and 200 degrees C / a moisture absorption expansion coefficient, and / in Tg / 200 degrees C or more, and 300 degrees-C or more temperature of 400 degrees C or less] to be 200 or more MPas into the contents. 20% or more at the time of 4.5 - 8.5GPa and fracture. [10 ppm or less]

[0018] The place made into the summary of the manufacture approach of the polyimide film of this invention 4 and 4'-diamino diphenyl ether is dissolved into an organic solvent. pyromellitic acid 2 anhydride, 3, 3', 4, and 4' - benzophenone tetracarboxylic dianhydride -- One chosen from 3, 3', and 4 and the group which consists of 4'-biphenyl tetracarboxylic dianhydride is added. Then, p-phenylene diamine is added, the dehydration ring closure of the polyamide acid polymer which added oxy-JIFUTARU acid 2 anhydride and was obtained is continuously added p-phenylene screw (trimellitic acid monoester anhydride) and carried out to this organic solvent solution, and it makes to obtain a polyimide film into the contents.

[0019] The place made into other summaries of the manufacture approach of the polyimide film of this invention p-phenylene diamine is dissolved into an organic solvent -- making (pyromellitic acid -- 2 anhydride) One chosen from 3, 3', and the group that consists of - benzophenone tetracarboxylic dianhydride, 3, 3', and 4 and 4' 4, 4'-biphenyl tetracarboxylic dianhydride is added. Then, p-phenylene screw (trimellitic acid monoester anhydride) is added. The dehydration ring closure of the polyamide acid polymer which added oxy-JIFUTARU acid 2 anhydride and was obtained is continuously added 4 and 4'-diamino diphenyl ether and carried out to this organic solvent solution using an acid anhydride and the third class amine, and it makes to obtain a polyimide film into the contents.

[0020]

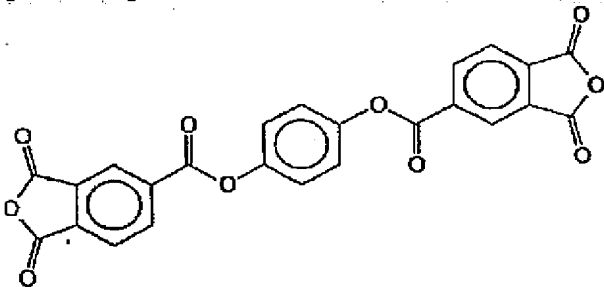
[Embodiment of the Invention] Hereafter, the polyimide film concerning this invention is explained based on one example of the gestalt of the operation. In addition, the vocabulary "a monomer" of this invention means the diamine of a monomer, or either of tetracarboxylic dianhydride.

[0021] The polyimide film concerning this invention may be manufactured from the polyamide acid prepared by this contractor with the well-known polyamide acid synthesis method. Preferably, by the manufacture approach of the polyimide film of this invention, the above-mentioned dehydration ring closure may be performed under existence of the imide-ized agent of an acid anhydride and a tertiary amine.

[0022] p-phenylene screw which has the following structure expressions especially as acid 2 anhydride in this invention in order to compound a polyamide acid (trimellitic acid monoester anhydride) (henceforth TMHQ)

[0023]

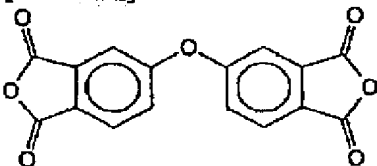
[Formula 1]



[0024] And oxy-JIFUTARU acid 2 anhydride with the following structure expressions (henceforth ODPA)

[0025]

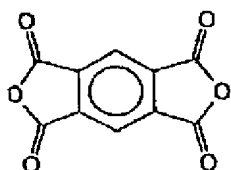
[Formula 2]



[0026] And pyromellitic acid 2 anhydride with the following structure expressions (henceforth PMDA)

[0027]

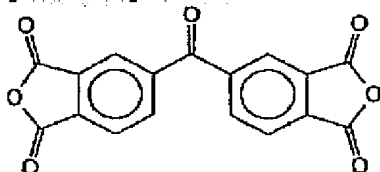
[Formula 3]



[0028] And 3 and 3' with the following structure expressions, 4, 4'-benzophenone tetracarboxylic dianhydride (henceforth BTDA)

[0029]

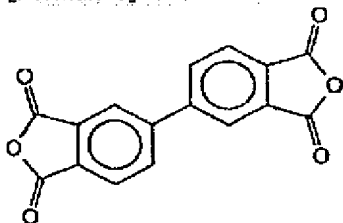
[Formula 4]



[0030] And 3 and 3' with the following structure expressions, 4, 4'-biphenyl tetracarboxylic dianhydride (henceforth BPDA)

[0031]

[Formula 5]



[0032] P-phenylene diamine which has the following structure expressions as diamine (henceforth PDA)

[0033]

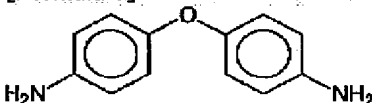
[Formula 6]



[0034] And 4 and 4'-diamino diphenyl ether with the following structure expressions (henceforth ODA)

[0035]

[Formula 7]



[0036] ***** The polyamide acid which can be used in order to manufacture the polyimide film which dissolves the above-mentioned monomer in an organic solvent, is made to carry out a polymerization reaction and is applied to this invention is obtained.

[0037] In combination with PDA, cylindrical structure is taken, the high elasticity of a film manifests itself, and since it is a principal chain structure top ester bond, it is lost from it being a little flexible thermally that coefficient of linear expansion falls of Following TMHQ extremely compared with the case where only pyromellitic acid is used, for example etc. Moreover, it also has the effectiveness that an ester bond eases polarization of an imide ring, lowers water absorption, and lowers the rate of swelling.

[0038] However, TMHQ is too hard structurally, and its coefficient of linear expansion is also still low, and its toughness of combination with PDA is inadequate. Also by copolymerizing diamino diphenyl ether, if it is still going to obtain the elastic modulus more than fixed, coefficient of linear expansion falls too much, and its toughness is also inadequate.

[0039] Using ODPA, the polymerization of PDA and the diamino diphenyl ether is carried out, and an inconvenient moderate coefficient of linear expansion which is not, sufficient toughness, etc. may be moderately realized in the combination of a high elastic modulus and copper. However, the configuration of this invention which the water absorption itself does not fall so much, lowers a moisture absorption property, and copolymerizes TMHQ further to keep many properties desirable is very effective only at ODPA.

[0040] Furthermore, the configuration of this invention which can newly give the high storage modulus of 200 or more MPas in 300-degree-C or more temperature of 400 degrees C or less, with other desirable properties held that it is realizable in the combination of ODPA and TMHQ by carrying out copolymerization of (the one chosen from the group which consists of PMDA, BTDA, and BPDA) is very effective.

[0041] The organic solvent used at the polymerization process of this invention can use well-known various solvents for this contractor. For example, although it is desirable to use the high polar solvents which have high solubility to a polyamide acid, it is also possible to add a poor solvent to these high polar solvents. As an example of high polar solvents, phenols, such as pyrrolidones, such as amides, such as N,N-dimethylformamide and N,N-dimethylacetamide, and a N-methyl-2-pyrrolidone, a phenol, p-chlorophenol, and o-chlorophenol, etc. are mentioned. As an example of a poor solvent, toluene, a tetrahydrofuran, an acetone, a methyl ethyl ketone, a methanol, ethanol, etc. are mentioned. Solubility can also be raised by mixing these solvents and adjusting a solubility parameter suitably.

[0042] The addition of the acid 2 above-mentioned anhydride and diamine the above-mentioned p-phenylene screw (trimellitic acid monoester anhydride) It is 1-90-mol % preferably. all acid 2 anhydride — receiving — 0 — many — the range not more than 90 mol % —

- oxy-JIFUTARU acid 2 anhydride — all acid 2 anhydride — receiving — less than [more than 9 85 mol %] — preferably 8-85-mol % — it is (pyromellitic acid 2 anhydride, 3, 3', 4, and 4' - benzophenone tetracarboxylic dianhydride —) One chosen from 3, 3', and 4 and the group which consists of 4'-biphenyl tetracarboxylic dianhydride all acid 2 anhydride — receiving — 1 — many — the range not more than 15 mol % — it is 2-14-mol % preferably, p-phenylene diamine is 25-90-mol % to all diamines, and 4 and 4'-diamino diphenyl ether is 10-75-mol % to all diamines.

[0043] Especially the addition sequence of each monomer for composition of a polyamide acid is not limited, but various approaches are possible for it. it is as it is about the further remaining tetracarboxylic dianhydride, dissolving all diamines, adding tetracarboxylic dianhydride to this gradually, considering as the equivalent in general, and adjusting viscosity to a solvent — it is — although dissolving in a suitable solvent, in addition making equivalent ratio equal is generally performed, it is not limited to this.

[0044] It is also possible to control the property of a film delicately depending on such addition sequence.

[0045] Dissolve ODA and PDA into a solvent, on the other hand (one chosen from the group which consists of PMDA, BTDA, and BPDA) is specifically added. Approach; which adds TMHQ succeedingly and adds ODA after that Or dissolve two sorts of diamines in the solvent similarly, and this is received. Approach; which adds (one chosen from the group which consists of PMDA, BTDA, and BPDA), and adds acid 2 matter of chance to this one by one in order of ODA and TMHQ succeedingly Or the method of dissolving two sorts of diamines similarly and adding the mixture of three sorts of acid 2 anhydrides to this; Either is dissolved in the solvent among two sorts of diamines. The approach of adding one sort chosen as this from three sorts of acid 2 anhydrides, adding one more sort of diamines after that, and adding two more sorts of acid 2 anhydrides after that further etc. can be raised.

[0046] If one sort of diamines are divided into two or more steps and it adds, a variation increases and the further delicate adjustment of various properties is still more possible for it by these. When the polyamide acid compounded by the procedure of adding (one chosen from the group which consists of PMDA, BTDA, and BPDA) to this by dissolving especially ODA into an organic solvent, adding PDA succeedingly, and adding TMHQ to this and adding ODA continuously is used, the polyimide film obtained rather than the case where the sequence which replaced above-mentioned ODA and PDA is adopted shows high Tg, and is desirable.

[0047] In any case, the sum total of the molar quantity of a diamine compound and the sum total of the molar quantity of an acid 2 anhydride compound are used so that it may become almost the same.

[0048] It is because polymerization degree goes up that it is completely the same too much, solution viscosity rises too much as a result and it is hard coming to deal with having presupposed "It is almost the same" here. It is the range of 0.98-1.02 preferably, and, as for especially the ratio of the diamine compound molar quantity sum total and the acid 2 anhydride compound molar quantity sum total, specifically, it is desirable 0.95-1.05, and that it is not 1:1.

[0049] Although especially the addition rate of each monomer is not limited, preferably TMHQ among [all] acid 2 anhydride It is less than [90 mol %] more mostly than zero-mol %. ODA It is less than [more than 9 mol %85 mol %], and (one chosen from the group which consists of PMDA, BTDA, and BPDA) is less than [more than 1 mol %15 mol %], PDA is less than [more than 25 mol %90 mol %] among [all] diamine, and ODA is less than [more than 10 mol %75 mol %].

[0050] Especially preferably, TMHQ is less than [more than 1 mol %90 mol %] among [all] acid 2 anhydride, ODA is less than [more than 8 mol %85 mol %], and (one chosen from the group which consists of PMDA, BTDA, and BPDA) is less than [more than 2 mol %14 mol %].

[0051] Most preferably, TMHQ is less than [more than 5 mol %50 mol %] among [all] acid 2 anhydride, ODA is less than [more than 47 mol %81 mol %], (one chosen from the group which consists of PMDA, BTDA, and BPDA) is less than [more than 3 mol %14 mol %], PDA is less than [more than 50 mol %90 mol %] among [all] diamine, and ODA is less than [more than 10 mol %50 mol %].

[0052] It is also possible to carry out delicate adjustment of the property of the polyimide film which small-quantity (amount not more than 10-mol-% of the whole diamine) —adds the monomer component of diamines other than five sorts of these monomers, and is obtained. Although based also on the monomer to be used, if it is copolymerization below this amount in general, a moisture absorption property, a heat characteristic, and a mechanical characteristic can be maintained at desirable level. As a monomer of the **** diamine for small quantity, halogenation objects, such as - bis(4-amino phenoxyphenyl) propane, and dimethyl benzidine, 2, and 2', 4, 4'-bis(4-amino phenoxy) biphenyls and these fluorines, etc. can be illustrated.

[0053] Although a polymerization reaction will not be especially limited if it is temperature generally used for the polymerization reaction of a polyamide acid, its 60 degrees C or less are desirable, and it is more desirable to carry out below 40 degrees C. When it becomes high temperature, it is easy to produce the ring opening reaction of an acid-anhydride radical, and the generation reaction of a polyamide acid may be checked.

[0054] Although it is desirable to make a polymerization reaction perform in inert gas, such as nitrogen or an argon, it can carry out also under other conditions.

[0055] Further 10 - 25wt% of the concentration in the solution of a polyamide acid is desirable 5 - 30wt%. If lower than this, solvents will increase in number, the desiccation after film manufacture takes time amount, in the case of concentration higher than this, viscosity may rise and processing may become difficult.

[0056] Although the viscosity of a polyamide acid solution will not be limited especially if it is the viscosity which can carry out film processing, it is 500-6000poise preferably about about 100-10000poise at 22 degrees C. It is also difficult to have a bad influence on the property of a film, if viscosity is too low, and to stabilize thickness in the case of processing. On the other hand, when viscosity is too high, in case stirring of a solution becomes difficult and processes it in the shape of a film, the strong force is needed, and it is inconvenient.

[0057] The solution of the obtained polyamide acid can be formed in the shape of a film, a polyamide acid can be imide-ized, and a polyimide film can be obtained. Generally, this imide-ization has the chemical approach using the thermal approach and dehydrating agent, or imide-ized catalyst which dehydrates with heating. Which approach of these may be used and the chemical approach and the thermal approach can also be used together. A dehydrating agent and a catalyst are added, according to the chemical approach heated and dried, it is more efficient than the thermal approach and the outstanding property may be given to a film. Although it is also possible to realize an equivalent property by putting in an extension process by the production process etc. if five sorts of monomers of the invention in this application are used even when not using a dehydrating agent or an imide-ized catalyst, the field of productivity to the chemical approach is desirable.

[0058] The dehydrating agents used for this invention are aliphatic series acid anhydrides, such as an acetic anhydride, an aromatic series acid anhydride, etc. Moreover, the catalysts used for imide-ization are tertiary amine, such as a pyridine, the alpha-picoline,

beta-picoline, gamma-picoline, a trimethylamine, dimethylaniline, triethylamine, and an isoquinoline, etc.

[0059] For example, although the example of the chemical approach of imide-izing is given to below, this invention is not limited to this. That is, the solution which added the dehydrating agent beyond a stoichiometry and the tertiary amine of the amount of catalysts to the obtained polyamide acid solution is cast or applied the shape of a film, a drum, or an endless belt made from organic compounds, such as a support plate and PET, and is made into the shape of film, the film is dried for [about 5 minutes -] 90 minutes at the temperature of 150 degrees C or less, and the paint film of a free-standing polyamide acid polymer is obtained. Next, this is torn off from a base material and an edge is fixed. Then, by heating gradually to 100 degrees C - about 500 degrees C, it is made to imide-ize, it removes from this after cooling, and a polyimide film is obtained.

[0060] The example of imide-izing by the thermal approach is not limited to this, although the same process as the above-mentioned chemical imide-ized method is mentioned. That is, a polyamide acid solution is cast or applied on base materials, such as a film made from organic compounds, such as a support plate and PET, a drum, or an endless belt, is made into the shape of film, and can be heat-treated.

[0061] On the occasion of manufacture of a film, further, a heat deterioration inhibitor is added and degradation of the film at the time of baking can be prevented. Other additives can be added and degradation of the film at the time of film manufacture etc. can also be prevented. As a heat deterioration inhibitor, or it has the degradation inhibitor of phosphoric-acid systems, such as triphenyl phosphate, and a substituent, the benzophenone which does not have a substituent is mentioned. As other additives, a metal-simple substance, an organometallic compound, or the fillers of textile glass yarn are mentioned.

[0062] The polyimide films concerning this invention manufactured as mentioned above are the rate of high elasticity, a high storage modulus, and a good polyimide film of the balance which has an elongation percentage, low coefficient of linear expansion, a low moisture absorption expansion coefficient, and each property at the time of high fracture, having fixed thermal resistance, an adhesive property, etc.

[0063] Specifically, the polyimide film concerning this invention can manifest itself the property that a storage modulus [in / elongation percentage / the time of 4.5 - 8.5GPa and fracture / modulus of elasticity in tension / 15-30 ppm and / mean coefficient of linear expansion / 100 degrees-C or more / mean coefficient of linear expansion 200 degrees C or less / a moisture absorption expansion coefficient 20% or more, and / in Tg / 200 degrees C or more, and 300 degrees-C or more temperature of 400 degrees C or less] is 200 or more MPas. [10 ppm or less]

[0064] Here, the property of the polyimide film concerning this invention is measured as follows. That is, an elongation percentage means the measured value which applied to ASTM-D882 correspondingly, respectively at the time of a modulus of elasticity in tension and fracture. Using TMAby SEIKO electronic industry incorporated company120C, an average coefficient of linear expansion raises temperature at a rate of 10 degrees C in the bottom of existence of nitrogen, and 1 minute, and measures and calculates the value at the time of 100 degrees C - 200 degrees C. A moisture-absorption coefficient of expansion is in the condition (it is about 3g to a 5mmx20mm sample) to which the minimum load was applied so that a polyimide film may not curtain, it is made to absorb moisture until it carries out gas conditioning of the humidity to 30RH% and is saturated completely, it measures a dimension, measures the back dimension which gas conditioning of the humidity was carried out [dimension] to 90RH%, and carried out saturation moisture absorption similarly after that, and asks for the rate of a dimensional change per 1% of relative-humidity differences from both result. Glass transition temperature (Tg) is measured being in **** mode and carrying out a temperature up at 3-degree-C a rate for /using a dynamic viscoelasticity measuring device (DMS200 by SEIKO electronic industry incorporated company).

[0065]

[Example] This invention is not limited by these examples although an example explains this invention more concretely below.

[0066] Under the ice bath in a nitrogen-purge ambient atmosphere, (Example 1) In dimethylacetamide 780g 33.4g (about 37.5-mol% in the total diamine) ODA is dissolved. Dissolve 3.9g (about four-mol% in total-acid 2 anhydride) PMDA, and 30.0g (about 62.5-mol% in the total diamine) PDA is dissolved. May add gradually TMHQ63.1g (about 31-mol% in total-acid 2 anhydride) to this, and it was made to stir and react, and ODPA89.6g (about 65-mol% in total-acid 2 anhydride) was added gradually continuously, and about 2500poise polyamide acid solution was obtained by measurement at 23 degrees C.

[0067] 100g of this polyamide acid solution - about 0 degree C - cooling - this - a 13.5g acetic anhydride and a 4.1g isoquinoline - in addition, homogeneity - stirring - after calcinating this on a SUS plate - 50 micrometers The cast was carried out to predetermined thickness are thin, and hot air drying was carried out at 125 degrees C for 5 minutes. After that, from the SUS plate, the film was torn off, where four pieces are fixed, it carried out at 250 degrees C by 170 degrees C for 1.5 minutes, and stoving of this was carried out at 430 degrees C by 350 degrees C for 3 minutes for 3 minutes for 1.5 minutes, and the polyimide film was obtained. The result of having measured an elongation percentage, coefficient of linear expansion, a moisture absorption expansion coefficient, Tg, and the storage modulus in 350 degrees C at the time of the modulus of elasticity in tension of this film and fracture is shown in Table 1.

[0068] Under the ice bath in a nitrogen-purge ambient atmosphere, (Example 2) In dimethylacetamide 780g 33.6g (about 37.5-mol% in the total diamine) ODA is dissolved. Dissolve 7.8g (about eight-mol% in total-acid 2 anhydride) PMDA, and 30.3g (about 62.5-mol% in the total diamine) PDA is dissolved. May add gradually TMHQ63.6g (about 31-mol% in total-acid 2 anhydride) to this, and it was made to stir and react, and ODPA84.7g (about 61-mol% in total-acid 2 anhydride) was added gradually continuously, and about 2500poise polyamide acid solution was obtained by measurement at 23 degrees C.

[0069] This polyamide acid solution was processed by the same approach as an example 1, and it considered as the polyimide film. The characteristic test was performed like the example 1. The result is shown in Table 1.

[0070] Under the ice bath in a nitrogen-purge ambient atmosphere, (Example 3) In dimethylacetamide 780g 33.9g (about 37.5-mol% in the total diamine) ODA is dissolved. 11.8g (about 12-mol% in total-acid 2 anhydride) PMDA is dissolved. 30.5g (about 62.5-mol% in the total diamine) PDA is dissolved. May add gradually TMHQ64.1g (about 31-mol% in total-acid 2 anhydride) to this, and it was made to stir and react, and ODPA79.8g (about 57-mol% in total-acid 2 anhydride) was added gradually continuously, and about 2500poise polyamide acid solution was obtained by measurement at 23 degrees C.

[0071] This polyamide acid solution was processed by the same approach as an example 1, and it considered as the polyimide film. The characteristic test was performed like the example 1. The result is shown in Table 1.

[0072] Under the ice bath in a nitrogen-purge ambient atmosphere, (Example 4) In dimethylacetamide 780g 33.1g (about 37.5-mol% in the total diamine) ODA is dissolved. Dissolve 7.1g (about five-mol% in total-acid 2 anhydride) BTDA, and 29.8g (about 62.5-mol% in the

total diamine) PDA is dissolved. May add gradually TMHQ62.6g (about 31-mol% in total-acid 2 anhydride) to this, and it was made to stir and react, and ODPA87.5g (about 64-mol% in total-acid 2 anhydride) was added gradually continuously, and about 2500poise polyamide acid solution was obtained by measurement at 23 degrees C.

[0073] This polyamide acid solution was processed by the same approach as an example 1, and it considered as the polyimide film. The characteristic test was performed like the example 1. The result is shown in Table 1.

[0074] Under the ice bath in a nitrogen-purge ambient atmosphere, (Example 5) In dimethylacetamide 780g 33.0g (about 37.5-mol% in the total diamine) ODA is dissolved. 17.7g (about 12.5-mol% in total-acid 2 anhydride) BTDA is dissolved. 29.7g (about 62.5-mol% in the total diamine) PDA is dissolved. May add gradually TMHQ62.5g (about 31-mol% in total-acid 2 anhydride) to this, and it was made to stir and react, and ODPA77.1g (about 56.5-mol% in total-acid 2 anhydride) was added gradually continuously, and about 2500poise polyamide acid solution was obtained by measurement at 23 degrees C.

[0075] This polyamide acid solution was processed by the same approach as an example 1, and it considered as the polyimide film. The characteristic test was performed like the example 1. The result is shown in Table 1.

[0076] (Example 6) Except [all] having made addition sequence of ODA and PDA reverse, the polymerization was performed by the same approach as an example 5, the polyimide film was produced by the same approach and the characteristic test was performed. The result is shown in Table 1.

[0077]

[Table 1]

	構成成分 (モル%)	引張弾性率 (GPa)	破断時 伸び率 (%)	線膨脹 係数 (ppm)	吸湿 膨脹係数 (ppm)	ガラス 転移温度 (°C)	350°Cでの 貯蔵弾性率 (MPa)
実施例1	ODA 37.5	6	30	21	6	240	210
	PMDA 4						
	PDA 62.5						
	TMHQ 31						
	ODPA 65						
実施例2	ODA 37.5	6	28	21	7	250	240
	PMDA 8						
	PDA 62.5						
	TMHQ 31						
	ODPA 61						
実施例3	ODA 37.5	6	30	20	7	255	270
	PMDA 12						
	PDA 62.5						
	TMHQ 31						
	ODPA 57						
実施例4	ODA 37.5	6	30	21	6	250	260
	BTDA 5						
	PDA 62.5						
	TMHQ 31						
	ODPA 64						
実施例5	ODA 37.5	6	28	21	7	260	310
	BTDA 12.5						
	PDA 62.5						
	TMHQ 31						
	ODPA 56.5						
実施例6	PDA 62.5	6	25	19	7	250	350
	BTDA 12.5						
	ODA 37.5						
	TMHQ 31						
	ODPA 56.5						
実施例7	PDA 62.5	6	25	21	7	275	360
	BTDA 12.5						
	TMHQ 31						
	ODA 37.5						
	ODPA 56.5						

[0078] Under the ice bath in a nitrogen-purge ambient atmosphere, (Example 7) In dimethylacetamide 780g 29.7g (about 62.5-mol% in the total diamine) PDA is dissolved. 17.7g (about 12.5-mol% in total-acid 2 anhydride) BTDA is dissolved. May add gradually TMHQ62.5g (about 31-mol% in total-acid 2 anhydride) to this, and a stirring reaction is carried out. ODA (33 and 0g (about 37.5-mol% in the total diamine)) was dissolved, ODPA77.1g (about 56.5-mol% in total-acid 2 anhydride) was added gradually continuously, and about 2500poise polyamide acid solution was obtained by measurement at 23 degrees C. This polyamide acid solution was processed by the same approach as an example 1, and it considered as the polyimide film. The characteristic test was performed like the example 1. The result is shown in Table 1.

[0079] (Examples 1-4 of a comparison) By the approach of adding acid 2 anhydride by the same approach as an example after dissolving all diamine components into dimethylacetamide, the polymerization reaction was performed so that it might become the total solid content concentration of 20% in a solution, and the viscosity of 2500poise. Each component and its mol % are shown in Table 2. A polyimide film is obtained using these polyamide acid solutions like an example, and the result of having measured the property is shown

in Table 2.

[0080]

[Table 2]

	構成成分 (モル%)	引張弾性率 (GPa)	破断時 伸び率 (%)	線膨張 係数 (ppm)	吸湿 膨張係数 (ppm)	ガラス 転移温度 (°C)	350°Cでの 貯蔵弾性率 (MPa)
比較例1	ODA 40 PDA 60 TMHQ 100	8.5	5	18	6	270	1000
比較例2	ODA 37.5 PDA 62.5 TMHQ 31 ODPA 69	6	30	23	5	255	150
比較例3	ODA 50 PDA 50 TMHQ 50 PMDA 50	5.5	20	9	6	350	1100

[0081]

[Effect of the Invention] the outstanding moisture absorption property which the polyimide film of this invention does not have in the old polyimide film for the bases, and especially low hygroscopic swelling — having — in addition — and without [therefore] being less than a copper coefficient of linear expansion, though it is high elasticity and a high storage modulus, when it uses as the substrate and the tape for TAB of ****, the extremely excellent curvature property can be discovered. Since the polyimide film of this invention is excellent also in flexibility and thermal resistance and does not spoil a property required as a base polyimide film, it can respond to the electronic equipment increasingly made minute.

[Translation done.]

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TECHNICAL FIELD

[Field of the Invention] This invention relates to the polyimide film excellent in the physical-properties balance which can give low curvature and high dimensional stability in a metal, especially a lamination product with copper.

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PRIOR ART

[Description of the Prior Art] The polyimide film is equipped with thermal resistance, insulation, solvent resistance, a low temperature performance-proof, etc., and is widely used for the computer list as an electrical-and-electric-equipment components ingredient of IC control.

[0003] In recent years, a computer list is asked for a miniaturization and thin shape-ization also for wiring substrates and an IC package ingredient with a miniaturization and thin-shape-izing of the electrical and electric equipment of IC control. For this reason, it is needed to be heating, to be tension, and that the dimensional change according to moisture absorption further is small also about the polyimide film with which the circuit pattern given to these also becomes minute, and is used for a flexible patchboard, the carrier tape for TAB, etc. Furthermore, it is necessary with thin-shape-izing of an ingredient to maintain the "elasticity" of the whole layered product and to make a processing process stability.

[0004] In order to fulfill such need, it is desired for coefficient of linear expansion of a polyimide film to be small, for an elastic modulus and a storage modulus to be high, and for a moisture absorption expansion coefficient to be low.

[0005] However, in order to make a polyimide film and copper foil rival and to process them in the case of manufacture of a flexible patchboard or an IC package, it is not desirable to differ from a copper coefficient of linear expansion greatly about film coefficient of linear expansion. That is, it is because curvature will arise in a lamination article, and it will be hard coming to carry out processing, consequently overall dimensional accuracy and the overall yield will fall, if the coefficient of linear expansion of a polyimide film and copper foil differs greatly. Therefore, what has the small difference of coefficient of linear expansion with copper foil is desirable.

[0006] Various attempts are made in order to obtain the polyimide film which has the above-mentioned property. First, for rate[of high elasticity]-izing of a polyimide film, it is known widely that what is necessary is just to use the monomer of upright structure, i.e., a monomer with high linearity. The coefficient of linear expansion of the ***** film for large quantities becomes low too much, and stops however, being suitable for the application of lamination with copper foil in a monomer with high linearity.

[0007] Though a comparatively high elastic modulus is realized, in order not to lower coefficient of linear expansion too much, using the monomer which has comparatively upright structure, not using a chemical imide-ized agent, it manufactures by the heat cure method, and there is also an example which takes the approach of making orientation of the direction of a field sweet. However, the heat cure method has the disadvantage that required heating time is long compared with the chemical cure method, and it is inferior to productivity.

[0008] Furthermore, if it is upright and a monomer with high linearity is used, generally, the flexibility of a film is spoiled and difficulty may produce it at the point which is one of the advantages as a flexible patchboard etc. that bending is possible.

[0009] Especially for a semiconductor package application, it is called for from a viewpoint of the dependability of a semi-conductor that water absorption is low as much as possible, and it is called for from a viewpoint of dimensional stability from it that a moisture absorption expansion coefficient is also low.

[0010] In order to lower water absorption and a moisture absorption expansion coefficient, it is effective to reduce the imide radical weight in the molecular structure. For this reason, the long-chain monomer which contains two or more crookedness radicals in a principal chain is used in many cases. However, as a result, decline in an elastic modulus and too much increase of coefficient of linear expansion are caused, and dimensional stability falls victim. When extreme, thermoplasticity which has Tg at low temperature 200 degrees C or less comes to be shown, and it stops being suitable for using as a base film. Moreover, when the long monomer was used with such linearity, packing of a chain could not become difficult, and sufficient toughness could not be discovered, but there were problems, like film-izing depending on the case itself becomes difficult.

[0011] Generally moreover, the value of the storage modulus of a viscoelastic body (a polyimide film is also contained) in the temperature field exceeding Tg, it becomes lower than the value of the storage modulus in ordinary temperature (a single figure). When the storage modulus in the temperature (for example, 300 degrees C or more 400 degrees C or less) which what figures about triple [2-] become low depending on the case is known, and is usually used for film production is extremely small, When a film curtains extremely in the temperature field of film production, it may become difficult to produce a flat film without sag itself.

[0012] As mentioned above, there were many points which should be taken [workability / of a film] into consideration besides these properties in order to realize all of the rate of high elasticity demanded as a property of a polyimide film, a high storage modulus, low coefficient of linear expansion, and the property of low absorptivity, and it was in the especially difficult situation to obtain the polyimide film with which there are problems, like other properties fall victim and it has a polyimide film and two or more good properties of all when it is going to satisfy one of properties.

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EFFECT OF THE INVENTION

[Effect of the Invention] the outstanding moisture absorption property which the polyimide film of this invention does not have in the old polyimide film for the bases, and especially low hygroscopic swelling -- having -- in addition -- and without [therefore] being less than a copper coefficient of linear expansion, though it is high elasticity and a high storage modulus, when it uses as the substrate and the tape for TAB of ***, the extremely excellent curvature property can be discovered. Since the polyimide film of this invention is excellent also in flexibility and thermal resistance and does not spoil a property required as a base polyimide film, it can respond to the electronic equipment increasingly made minute.

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TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] Then, this invention persons solved the above-mentioned trouble; and as a result of examining wholeheartedly manufacturing the polyimide film suitable for the flexible printed circuit board and TAB film of thin wiring which has many properties of all of the rate of high elasticity, a high storage modulus, the coefficient of linear expansion near copper, sufficient toughness, low water absorption, and a low moisture absorption expansion coefficient, they resulted in this invention.

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MEANS

[Means for Solving the Problem] this invention persons found out the polyimide film which can realize and control many property balance to altitude specifically, and its manufacture approach in the polyimide film of a specific presentation in view of the above-mentioned demand.

[0015] The place made into the summary of the polyimide film concerning this invention p-phenylene screw (trimellitic acid monoester anhydride), oxy-JIFUTARU acid 2 anhydride, pyromellitic acid 2 anhydride, 3, 3', 4, and 4' - benzophenone tetracarboxylic dianhydride - It makes into the contents to be manufactured from 3, 3', and the polyamide acid that one chosen from group which consists of - biphenyl tetracarboxylic dianhydride, p-phenylene diamine, and 4 and 4', 4'-diamino diphenyl ether is made to react in an organic solvent, and is obtained.

[0016] In said polyimide film the above-mentioned p-phenylene screw (trimellitic acid monoester anhydride) It is 1-90-mol % to all acid 2 anhydride. Oxy-JIFUTARU acid 2 anhydride all acid 2 anhydride -- receiving -- eight-mol % - 85-mol % -- it is (pyromellitic acid -- 2 anhydride) One chosen from 3, 3', and the group that consists of - benzophenone tetracarboxylic dianhydride, 3, 3', and 4 and 4', 4'-biphenyl tetracarboxylic dianhydride It makes to be %, for p-phenylene diamine to be 25-90-mol % to all diamines, and for 4 and 4'-diamino diphenyl ether to 2-14-mol be 10-75-mol % to all diamines into the contents to all acid 2 anhydride.

[0017] In the polyimide film to apply, it makes for a storage modulus [in / elongation percentage / modulus of elasticity in tension / 15-30 ppm and / mean coefficient of linear expansion / between 100 degrees C and 200 degrees C / a moisture absorption expansion coefficient, and / in Tg / 200 degrees C or more, and 300 degrees-C or more temperature of 400 degrees C or less] to be 200 or more MPas into the contents 20% or more at the time of 4.5 - 8.5GPa and fracture. [10 ppm or less]

[0018] The place made into the summary of the manufacture approach of the polyimide film of this invention 4 and 4'-diamino diphenyl ether is dissolved into an organic solvent, pyromellitic acid 2 anhydride, 3, 3', 4, and 4' - benzophenone tetracarboxylic dianhydride -- One chosen from 3, 3', and 4 and the group which consists of 4'-biphenyl tetracarboxylic dianhydride is added. Then, p-phenylene diamine is added, the dehydration ring closure of the polyamide acid polymer which added oxy-JIFUTARU acid 2 anhydride and was obtained is continuously added p-phenylene screw (trimellitic acid monoester anhydride) and carried out to this organic solvent solution, and it makes to obtain a polyimide film into the contents.

[0019] The place made into other summaries of the manufacture approach of the polyimide film of this invention p-phenylene diamine is dissolved into an organic solvent -- making (pyromellitic acid -- 2 anhydride) One chosen from 3, 3', and the group that consists of - benzophenone tetracarboxylic dianhydride, 3, 3', and 4 and 4', 4'-biphenyl tetracarboxylic dianhydride is added. Then, p-phenylene screw (trimellitic acid monoester anhydride) is added. The dehydration ring closure of the polyamide acid polymer which added oxy-JIFUTARU acid 2 anhydride and was obtained is continuously added 4 and 4'-diamino diphenyl ether and carried out to this organic solvent solution using an acid anhydride and the third class amine, and it makes to obtain a polyimide film into the contents.

[0020]

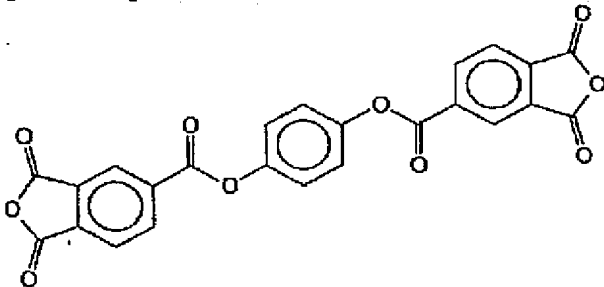
[Embodiment of the Invention] Hereafter, the polyimide film concerning this invention is explained based on one example of the gestalt of the operation. In addition, the vocabulary "a monomer" of this invention means the diamine of a monomer, or either of tetracarboxylic dianhydride.

[0021] The polyimide film concerning this invention may be manufactured from the polyamide acid prepared by this contractor with the well-known polyamide acid synthesis method. Preferably, by the manufacture approach of the polyimide film of this invention, the above-mentioned dehydration ring closure may be performed under existence of the imide-ized agent of an acid anhydride and a tertiary amine.

[0022] p-phenylene screw which has the following structure expressions especially as acid 2 anhydride in this invention in order to compound a polyamide acid (trimellitic acid monoester anhydride) (henceforth TMHQ)

[0023]

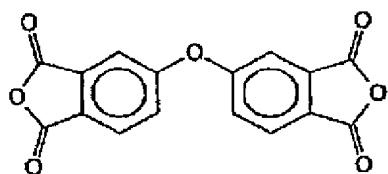
[Formula 1]



[0024] And oxy-JIFUTARU acid 2 anhydride with the following structure expressions (henceforth ODPA)

[0025]

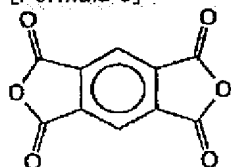
[Formula 2]



[0026] And pyromellitic acid 2 anhydride with the following structure expressions (henceforth PMDA)

[0027]

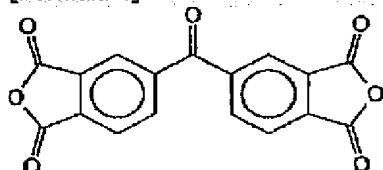
[Formula 3]



[0028] And 3 and 3' with the following structure expressions, 4, 4'-benzophenone tetracarboxylic dianhydride (henceforth BTDA)

[0029]

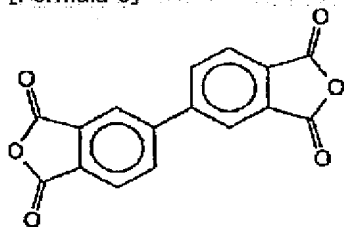
[Formula 4]



[0030] And 3 and 3' with the following structure expressions, 4, 4'-biphenyl tetracarboxylic dianhydride (henceforth BPDA)

[0031]

[Formula 5]



[0032] P-phenylene diamine which has the following structure expressions as diamine (henceforth PDA)

[0033]

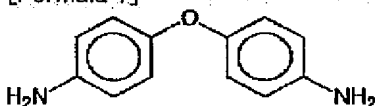
[Formula 6]



[0034] And 4 and 4'-diamino diphenyl ether with the following structure expressions (henceforth ODA)

[0035]

[Formula 7]



[0036] ***** The polyamide acid which can be used in order to manufacture the polyimide film which dissolves the above-mentioned monomer in an organic solvent, is made to carry out a polymerization reaction and is applied to this invention is obtained.

[0037] In combination with PDA, cylindrical structure is taken, the high elasticity of a film manifests itself, and since it is a principal chain structure top ester bond, it is lost from it being a little flexible thermally that coefficient of linear expansion falls of Following TMHQ extremely compared with the case where only pyromellitic acid is used, for example etc. Moreover, it also has the effectiveness that an ester bond eases polarization of an imide ring, lowers water absorption, and lowers the rate of swelling.

[0038] However, TMHQ is too hard structurally, and its coefficient of linear expansion is also still low, and its toughness of combination with PDA is inadequate. Also by copolymerizing diamino diphenyl ether, if it is still going to obtain the elastic modulus more than fixed, coefficient of linear expansion falls too much, and its toughness is also inadequate.

[0039] Using ODPA, the polymerization of PDA and the diamino diphenyl ether is carried out, and an inconvenient moderate coefficient of linear expansion which is not, sufficient toughness, etc. may be moderately realized in the combination of a high elastic modulus and copper. However, the configuration of this invention which the water absorption itself does not fall so much, lowers a moisture absorption property, and copolymerizes TMHQ further to keep many properties desirable is very effective only at ODPA.

[0040] Furthermore, the configuration of this invention which can newly give the high storage modulus of 200 or more MPas in 300-degree-C or more temperature of 400 degrees C or less, with other desirable properties held that it is realizable in the combination of ODPA and TMHQ by carrying out copolymerization of (the one chosen from the group which consists of PMDA, BTDA, and BPDA) is

very effective.

[0041] The organic solvent used at the polymerization process of this invention can use well-known various solvents for this contractor. For example, although it is desirable to use the high polar solvents which have high solubility to a polyamide acid, it is also possible to add a poor solvent to these high polar solvents. As an example of high polar solvents, phenols, such as pyrrolidones, such as amides, such as N,N-dimethylformamide and N,N-dimethylacetamide, and a N-methyl-2-pyrrolidone, a phenol, p-chlorophenol, and o-chlorophenol, etc. are mentioned. As an example of a poor solvent, toluene, a tetrahydrofuran, an acetone, a methyl ethyl ketone, a methanol, ethanol, etc. are mentioned. Solubility can also be raised by mixing these solvents and adjusting a solubility parameter suitably.

[0042] The addition of the acid 2 above-mentioned anhydride and diamine the above-mentioned p-phenylene screw (trimellitic acid monoester anhydride) It is 1-90-mol % preferably. all acid 2 anhydride — receiving — 0 — many — the range not more than 90 mol % — oxy-JIFUTARU acid 2 anhydride — all acid 2 anhydride — receiving — less than [more than 9 85 mol %] — preferably 8-85-mol % — it is (pyromellitic acid 2 anhydride, 3, 3', 4, and 4' - benzophenone tetracarboxylic dianhydride —) One chosen from 3, 3', and 4 and the group which consists of 4'-biphenyl tetracarboxylic dianhydride all acid 2 anhydride — receiving — 1 — many — the range not more than 15 mol % — it is 2-14-mol % preferably, p-phenylene diamine is 25-90-mol % to all diamines, and 4 and 4'-diamino diphenyl ether is 10-75-mol % to all diamines.

[0043] Especially the addition sequence of each monomer for composition of a polyamide acid is not limited, but various approaches are possible for it, it is as it is about the further remaining tetracarboxylic dianhydride, dissolving all diamines, adding tetracarboxylic dianhydride to this gradually, considering as the equivalent in general, and adjusting viscosity to a solvent — it is — although dissolving in a suitable solvent, in addition making equivalent ratio equal is generally performed, it is not limited to this.

[0044] It is also possible to control the property of a film delicately depending on such addition sequence.

[0045] Dissolve ODA and PDA into a solvent, on the other hand (one chosen from the group which consists of PMDA, BTDA, and BPDA) is specifically added. Approach; which adds TMHQ succeedingly and adds ODPA after that Or dissolve two sorts of diamines in the solvent similarly, and this is received. Approach; which adds (one chosen from the group which consists of PMDA, BTDA, and BPDA), and adds acid 2 matter of chance to this one by one in order of ODPA and TMHQ succeedingly Or the method of dissolving two sorts of diamines similarly and adding the mixture of three sorts of acid 2 anhydrides to this; Either is dissolved in the solvent among two sorts of diamines. The approach of adding one sort chosen as this from three sorts of acid 2 anhydrides; adding one more sort of diamines after that, and adding two more sorts of acid 2 anhydrides after that further etc. can be raised.

[0046] If one sort of diamines are divided into two or more steps and it adds, a variation increases and the further delicate adjustment of various properties is still more possible for it by these. When the polyamide acid compounded by the procedure of adding (one chosen from the group which consists of PMDA, BTDA, and BPDA) to this by dissolving especially ODA into an organic solvent, adding PDA succeedingly, and adding TMHQ to this and adding ODPA continuously is used, the polyimide film obtained rather than the case where the sequence which replaced above-mentioned ODA and PDA is adopted shows high Tg, and is desirable.

[0047] In any case, the sum total of the molar quantity of a diamine compound and the sum total of the molar quantity of an acid 2 anhydride compound are used so that it may become almost the same.

[0048] It is because polymerization degree goes up that it is completely the same too much, solution viscosity rises too much as a result and it is hard coming to deal with having presupposed "It is almost the same" here. It is the range of 0.98-1.02 preferably, and, as for especially the ratio of the diamine compound molar quantity sum total and the acid 2 anhydride compound molar quantity sum total, specifically, it is desirable 0.95-1.05, and that it is not 1:1.

[0049] Although especially the addition rate of each monomer is not limited, preferably TMHQ among [all] acid 2 anhydride It is less than [90 mol %] more mostly than zero-mol %. ODPA It is less than [more than 9 mol %85 mol %], and (one chosen from the group which consists of PMDA, BTDA, and BPDA) is less than [more than 1 mol %15 mol %], PDA is less than [more than 25 mol %90 mol %] among [all] diamine, and ODA is less than [more than 10 mol %75 mol %].

[0050] Especially preferably, TMHQ is less than [more than 1 mol %90 mol %] among [all] acid 2 anhydride, ODPA is less than [more than 8 mol %85 mol %], and (one chosen from the group which consists of PMDA, BTDA, and BPDA) is less than [more than 2 mol %14 mol %].

[0051] Most preferably, TMHQ is less than [more than 5 mol %50 mol %] among [all] acid 2 anhydride, ODPA is less than [more than 47 mol %81 mol %], (one chosen from the group which consists of PMDA, BTDA, and BPDA) is less than [more than 3 mol %14 mol %], PDA is less than [more than 50 mol %90 mol %] among [all] diamine, and ODA is less than [more than 10 mol %50 mol %].

[0052] It is also possible to carry out delicate adjustment of the property of the polyimide film which small-quantity(amount not more than 10-mol-% of the whole diamine)-adds the monomer component of diamines other than five sorts of these monomers, and is obtained. Although based also on the monomer to be used, if it is copolymerization below this amount in general, a moisture absorption property, a heat characteristic, and a mechanical characteristic can be maintained at desirable level. As a monomer of the **** diamine for small quantity, halogenation objects, such as - bis(4-amino phenoxyphenyl) propane, and dimethyl benzidine, 2, and 2 '4, 4'-bis(4-amino phenoxy) biphenyls and these fluorines, etc. can be illustrated.

[0053] Although a polymerization reaction will not be especially limited if it is temperature generally used for the polymerization reaction of a polyamide acid, its 60 degrees C or less are desirable, and it is more desirable to carry out below 40 degrees C. When it becomes high temperature, it is easy to produce the ring opening reaction of an acid-anhydride radical, and the generation reaction of a polyamide acid may be checked.

[0054] Although it is desirable to make a polymerization reaction perform in inert gas, such as nitrogen or an argon, it can carry out also under other conditions.

[0055] Further 10 - 25wt% of the concentration in the solution of a polyamide acid is desirable 5 - 30wt%. If lower than this, solvents will increase in number, the desiccation after film manufacture takes time amount, in the case of concentration higher than this, viscosity may rise and processing may become difficult.

[0056] Although the viscosity of a polyamide acid solution will not be limited especially if it is the viscosity which can carry out film processing, it is 500-6000poise preferably about about 100-10000poise at 22 degrees C. It is also difficult to have a bad influence on the property of a film, if viscosity is too low, and to stabilize thickness in the case of processing. On the other hand, when viscosity is too high, in case stirring of a solution becomes difficult and processes it in the shape of a film, the strong force is needed, and it is inconvenient.

[0057] The solution of the obtained polyamide acid can be formed in the shape of a film, a polyamide acid can be imide-ized, and a polyimide film can be obtained. Generally, this imide-ization has the chemical approach using the thermal approach and dehydrating agent, or imide-ized catalyst which dehydrates with heating. Which approach of these may be used and the chemical approach and the thermal approach can also be used together. A dehydrating agent and a catalyst are added, according to the chemical approach heated and dried, it is more efficient than the thermal approach and the outstanding property may be given to a film. Although it is also possible to realize an equivalent property by putting in an extension process by the production process etc. if five sorts of monomers of the invention in this application are used even when not using a dehydrating agent or an imide-ized catalyst, the field of productivity to the chemical approach is desirable.

[0058] The dehydrating agents used for this invention are aliphatic series acid anhydrides, such as an acetic anhydride, an aromatic series acid anhydride, etc. Moreover, the catalysts used for imide-ization are tertiary amine, such as a pyridine, the alpha-picoline, beta-picoline, gamma-picoline, a trimethylamine, dimethylaniline, triethylamine, and an isoquinoline, etc.

[0059] For example, although the example of the chemical approach of imide-izing is given to below, this invention is not limited to this. That is, the solution which added the dehydrating agent beyond a stoichiometry and the tertiary amine of the amount of catalysts to the obtained polyamide acid solution is cast or applied the shape of a film, a drum, or an endless belt made from organic compounds, such as a support plate and PET, and is made into the shape of film, the film is dried for [about 5 minutes -] 90 minutes at the temperature of 150 degrees C or less, and the paint film of a free-standing polyamide acid polymer is obtained. Next, this is torn off from a base material and an edge is fixed. Then, by heating gradually to 100 degrees C - about 500 degrees C, it is made to imide-ize, it removes from this after cooling, and a polyimide film is obtained.

[0060] The example of imide-izing by the thermal approach is not limited to this, although the same process as the above-mentioned chemical imide-ized method is mentioned. That is, a polyamide acid solution is cast or applied on base materials, such as a film made from organic compounds, such as a support plate and PET, a drum, or an endless belt, is made into the shape of film, and can be heat-treated.

[0061] On the occasion of manufacture of a film, further, a heat deterioration inhibitor is added and degradation of the film at the time of baking can be prevented. Other additives can be added and degradation of the film at the time of film manufacture etc. can also be prevented. As a heat deterioration inhibitor, or it has the degradation inhibitor of phosphoric-acid systems, such as triphenyl phosphate, and a substituent, the benzophenone which does not have a substituent is mentioned. As other additives, a metal simple substance, an organometallic compound, or the fillers of textile glass yarn are mentioned.

[0062] The polyimide films concerning this invention manufactured as mentioned above are the rate of high elasticity, a high storage modulus, and a good polyimide film of the balance which has an elongation percentage, low coefficient of linear expansion, a low moisture absorption expansion coefficient, and each property at the time of high fracture, having fixed thermal resistance, an adhesive property, etc.

[0063] Specifically, the polyimide film concerning this invention can manifest itself the property that a storage modulus [in / elongation percentage / the time of 4.5 - 8.5GPa and fracture / modulus of elasticity in tension / 15-30 ppm and / mean coefficient of linear expansion / 100 degrees-C or more / mean coefficient of linear expansion 200 degrees C or less / a moisture absorption expansion coefficient 20% or more, and / in Tg / 200 degrees C or more, and 300 degrees-C or more temperature of 400 degrees C or less] is 200 or more MPas. [10 ppm or less]

[0064] Here, the property of the polyimide film concerning this invention is measured as follows. That is, an elongation percentage means the measured value which applied to ASTM-D882 correspondingly, respectively at the time of a modulus of elasticity in tension and fracture. Using TMAby SEIKO electronic industry incorporated company120C, an average coefficient of linear expansion raises temperature at a rate of 10 degrees C in the bottom of existence of nitrogen, and 1 minute, and measures and calculates the value at the time of 100 degrees C - 200 degrees C. A moisture-absorption coefficient of expansion is in the condition (it is about 3g to a 5mmx20mm sample) to which the minimum load was applied so that a polyimide film may not curtain, it is made to absorb moisture until it carries out gas conditioning of the humidity to 30RH% and is saturated completely, it measures a dimension, measures the back dimension which gas conditioning of the humidity was carried out [dimension] to 90RH%, and carried out saturation moisture absorption similarly after that, and asks for the rate of a dimensional change per 1% of relative-humidity differences from both result. Glass transition temperature (Tg) is measured being in **** mode and carrying out a temperature up at 3-degree-C a rate for /using a dynamic viscoelasticity measuring device (DMS200 by SEIKO electronic industry incorporated company).

[Translation done.]

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- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.*** shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

EXAMPLE

[Example] This invention is not limited by these examples although an example explains this invention more concretely below.

[0066] Under the ice bath in a nitrogen-purge ambient atmosphere, (Example 1) In dimethylacetamide 780g 33.4g (about 37.5-mol% in the total diamine) ODA is dissolved. Dissolve 3.9g (about four-mol% in total-acid 2 anhydride) PMDA, and 30.0g (about 62.5-mol% in the total diamine) PDA is dissolved. May add gradually TMHQ63.1g (about 31-mol% in total-acid 2 anhydride) to this, and it was made to stir and react, and ODP89.6g (about 65-mol% in total-acid 2 anhydride) was added gradually continuously, and about 2500poise polyamide acid solution was obtained by measurement at 23 degrees C.

[0067] 100g of this polyamide acid solution — about 0 degree C — cooling — this — a 13.5g acetic anhydride and a 4.1g isoquinoline — in addition, homogeneity — stirring — after calcinating this on an SUS plate — 50 micrometers The cast was carried out to predetermined thickness are thin, and hot air drying was carried out at 125 degrees C for 5 minutes. After that, from the SUS plate, the film was torn off; where four pieces are fixed, it carried out at 250 degrees C by 170 degrees C for 1.5 minutes, and stoving of this was carried out at 430 degrees C by 350 degrees C for 3 minutes for 3 minutes for 1.5 minutes, and the polyimide film was obtained. The result of having measured an elongation percentage, coefficient of linear expansion, a moisture absorption expansion coefficient, Tg, and the storage modulus in 350 degrees C at the time of the modulus of elasticity in tension of this film and fracture is shown in Table 1.

[0068] Under the ice bath in a nitrogen-purge ambient atmosphere, (Example 2) In dimethylacetamide 780g 33.6g (about 37.5-mol% in the total diamine) ODA is dissolved. Dissolve 7.8g (about eight-mol% in total-acid 2 anhydride) PMDA, and 30.3g (about 62.5-mol% in the total diamine) PDA is dissolved. May add gradually TMHQ63.6g (about 31-mol% in total-acid 2 anhydride) to this, and it was made to stir and react, and ODP84.7g (about 61-mol% in total-acid 2 anhydride) was added gradually continuously, and about 2500poise polyamide acid solution was obtained by measurement at 23 degrees C.

[0069] This polyamide acid solution was processed by the same approach as an example 1, and it considered as the polyimide film. The characteristic test was performed like the example 1. The result is shown in Table 1.

[0070] Under the ice bath in a nitrogen-purge ambient atmosphere, (Example 3) In dimethylacetamide 780g 33.9g (about 37.5-mol% in the total diamine) ODA is dissolved. 11.8g (about 12-mol% in total-acid 2 anhydride) PMDA is dissolved. 30.5g (about 62.5-mol% in the total diamine) PDA is dissolved. May add gradually TMHQ64.1g (about 31-mol% in total-acid 2 anhydride) to this, and it was made to stir and react, and ODP87.8g (about 57-mol% in total-acid 2 anhydride) was added gradually continuously, and about 2500poise polyamide acid solution was obtained by measurement at 23 degrees C.

[0071] This polyamide acid solution was processed by the same approach as an example 1, and it considered as the polyimide film. The characteristic test was performed like the example 1. The result is shown in Table 1.

[0072] Under the ice bath in a nitrogen-purge ambient atmosphere, (Example 4) In dimethylacetamide 780g 33.1g (about 37.5-mol% in the total diamine) ODA is dissolved. Dissolve 7.1g (about five-mol% in total-acid 2 anhydride) BTDA, and 29.8g (about 62.5-mol% in the total diamine) PDA is dissolved. May add gradually TMHQ62.6g (about 31-mol% in total-acid 2 anhydride) to this, and it was made to stir and react, and ODP87.5g (about 64-mol% in total-acid 2 anhydride) was added gradually continuously, and about 2500poise polyamide acid solution was obtained by measurement at 23 degrees C.

[0073] This polyamide acid solution was processed by the same approach as an example 1, and it considered as the polyimide film. The characteristic test was performed like the example 1. The result is shown in Table 1.

[0074] Under the ice bath in a nitrogen-purge ambient atmosphere, (Example 5) In dimethylacetamide 780g 33.0g (about 37.5-mol% in the total diamine) ODA is dissolved. 17.7g (about 12.5-mol% in total-acid 2 anhydride) BTDA is dissolved. 29.7g (about 62.5-mol% in the total diamine) PDA is dissolved. May add gradually TMHQ62.5g (about 31-mol% in total-acid 2 anhydride) to this, and it was made to stir and react, and ODP87.1g (about 56.5-mol% in total-acid 2 anhydride) was added gradually continuously, and about 2500poise polyamide acid solution was obtained by measurement at 23 degrees C.

[0075] This polyamide acid solution was processed by the same approach as an example 1, and it considered as the polyimide film. The characteristic test was performed like the example 1. The result is shown in Table 1.

[0076] (Example 6) Except [all] having made addition sequence of ODA and PDA reverse, the polymerization was performed by the same approach as an example 5, the polyimide film was produced by the same approach and the characteristic test was performed. The result is shown in Table 1.

[0077]

[Table 1]

	構成成分 (モル%)	引張弾性率 (GPa)	破断時 伸び率 (%)	線膨脹 係数 (ppm)	吸湿 膨脹係数 (ppm)	ガラス 転移温度 (°C)	350°Cでの 貯蔵弾性率 (MPa)
実施例1	ODA 37.5	6	30	21	6	240	210
	PMDA 4						
	PDA 62.5						
	TMHQ 31						
	ODPA 65						
実施例2	ODA 37.5	6	28	21	7	250	240
	PMDA 8						
	PDA 62.5						
	TMHQ 31						
	ODPA 61						
実施例3	ODA 37.5	6	30	20	7	255	270
	PMDA 12						
	PDA 62.5						
	TMHQ 31						
	ODPA 57						
実施例4	ODA 37.5	6	30	21	6	250	260
	BTDA 5						
	PDA 62.5						
	TMHQ 31						
	ODPA 64						
実施例5	ODA 37.5	6	28	21	7	260	310
	BTDA 12.5						
	PDA 62.5						
	TMHQ 31						
	ODPA 56.5						
実施例6	PDA 62.5	6	25	19	7	250	350
	BTDA 12.5						
	ODA 37.5						
	TMHQ 31						
	ODPA 56.5						
実施例7	PDA 62.5	6	25	21	7	275	360
	BTDA 12.5						
	TMHQ 31						
	ODA 37.5						
	ODPA 56.5						

[0078] Under the ice bath in a nitrogen-purge ambient atmosphere, (Example 7) In dimethylacetamide 780g 29.7g (about 62.5-mol% in the total diamine) PDA is dissolved. 17.7g (about 12.5-mol% in total-acid 2 anhydride) BTDA is dissolved. May add gradually TMHQ62.5g (about 31-mol% in total-acid 2 anhydride) to this, and a stirring reaction is carried out. ODA (33 and 0g (about 37.5-mol% in the total diamine)) was dissolved, ODPA77.1g (about 56.5-mol% in total-acid 2 anhydride) was added gradually continuously, and about 2500poise polyamide acid solution was obtained by measurement at 23 degrees C. This polyamide acid solution was processed by the same approach as an example 1, and it considered as the polyimide film. The characteristic test was performed like the example 1. The result is shown in Table 1.

[0079] (Examples 1-4 of a comparison) By the approach of adding acid 2 anhydride by the same approach as an example after dissolving all diamine components into dimethylacetamide, the polymerization reaction was performed so that it might become the total solid content concentration of 20% in a solution, and the viscosity of 2500poise. Each component and its mol % are shown in Table 2. A polyimide film is obtained using these polyamide acid solutions like an example, and the result of having measured the property is shown in Table 2.

[0080]

[Table 2]

	構成成分 (モル%)	引張弾性率 (GPa)	破断時 伸び率 (%)	線膨脹 係数 (ppm)	吸湿 膨脹係数 (ppm)	ガラス 転移温度 (°C)	350°Cでの 貯蔵弾性率 (MPa)
比較例1	ODA 40	8.5	5	18	6	270	1000
	PDA 60						
	TMHQ 100						
比較例2	ODA 37.5	6	30	23	5	255	150
	PDA 62.5						
	TMHQ 31						
	ODPA 69						
比較例3	ODA 50	5.5	20	9	6	350	1100
	PDA 50						
	TMHQ 50						
	PMDA 50						

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(54) 【発明の名称】 ポリイミドフィルムおよびその製造方法

(57) 【要約】

【課題】 高弾性、高貯蔵弾性率、高伸び率、銅箔と同等の低線膨張係数、低吸湿膨張係数とを兼ね備える優れたポリイミドフィルムを得ることを目的とする。

【解決手段】 p-フェニレンビス (トリメリット酸モノエステル無水物)、オキシジフタル酸二無水物、p-フェニレンジアミン、4,4'-ジアミノジフェニルエーテル、及び (ピロメリット酸二無水物、3,3',4,4'-ベンゾフェノンテトラカルボン酸二無水物、3,3',4,4'-ビフェニルテトラカルボン酸二無水物からなる群から選択される1つの酸二無水物) を有機溶剤中で反応させて得られるポリアミド酸からポリイミドフィルムを製造する。

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【特許請求の範囲】

【請求項1】 p-フェニレンビス（トリメリット酸モノエステル無水物）と、オキシジフタル酸二無水物と、p-フェニレンジアミンと、4, 4'-ジアミノジフェニルエーテルと、および（ピロメリット酸二無水物、3, 3', 4, 4'-ベンゾフェノンテトラカルボン酸二無水物、3, 3', 4, 4'-ビフェニルテトラカルボン酸二無水物からなる群から選択される1つ）で構成される5種のモノマーを有機溶剤中で反応させて得られるポリイミド酸から製造されることを特徴とするポリイミドフィルム。

【請求項2】 前記ポリイミド酸から製造されるポリイミドフィルムにおいて、前記モノマーの添加量が、p-フェニレンビス（トリメリット酸モノエステル無水物）が、全酸二無水物に対して1~90モル%であり、オキシジフタル酸二無水物が、全酸二無水物に対して8~85モル%であり、（ピロメリット酸二無水物、3, 3', 4, 4'-ベンゾフェノンテトラカルボン酸二無水物、3, 3', 4, 4'-ビフェニルテトラカルボン酸二無水物からなる群から選択される1つ）が、全酸二無水物に対して2~14モル%であり、p-フェニレンジアミンが、全ジアミンに対して25~90モル%であり、4, 4'-ジアミノジフェニルエーテルが、全ジアミンに対して10~75モル%であることを特徴とする請求項1に記載のポリイミドフィルム。

【請求項3】 請求項1または請求項2に記載されるポリイミドフィルムであって、100℃以上200℃以下の平均線膨張係数が15~30ppm、引張弾性率が4.5~8.5GPa、破断時伸び率が20%以上、吸湿膨張係数が10ppm以下、T_gが200℃以上、300℃以上400℃以下の温度における貯蔵弾性率が200MPa以上であることを特徴とするポリイミドフィルム。

【請求項4】 4, 4'-ジアミノジフェニルエーテルを有機溶剤中に溶解させ、（ピロメリット酸二無水物、3, 3', 4, 4'-ベンゾフェノンテトラカルボン酸二無水物、3, 3', 4, 4'-ビフェニルテトラカルボン酸二無水物からなる群から選択される1つ）を加え、続いてp-フェニレンジアミンを加え、該有機溶剤溶液にp-フェニレンビス（トリメリット酸モノエステル無水物）を加え、続いてオキシジフタル酸二無水物を加えて得られたポリイミド酸重合体を、酸無水物と第三級アミンとを用いて脱水閉環し、ポリイミドフィルムを得ることを特徴とするポリイミドフィルムの製造方法。

【請求項5】 p-フェニレンジアミンを有機溶剤中に溶解させ、（ピロメリット酸二無水物、3, 3', 4, 4'-ベンゾフェノンテトラカルボン酸二無水物、3, 3', 4, 4'-ビフェニルテトラカルボン酸二無水物からなる群から選択される1つ）を加え、続いて、p-フェニレンビス（トリメリット酸モノエステル無水物）

を加え、該有機溶剤溶液に4, 4'-ジアミノジフェニルエーテルを加え、続いてオキシジフタル酸二無水物を加えて得られたポリイミド酸重合体を、酸無水物と第三級アミンとを用いて脱水閉環し、ポリイミドフィルムを得ることを特徴とするポリイミドフィルムの製造方法。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】 本発明は、金属、特に銅との張り合わせ製品において、低反り、高寸法安定性を与え得る、物性バランスに優れたポリイミドフィルムに関する。

【0002】

【従来の技術】 ポリイミドフィルムは、耐熱性、絶縁性、耐溶剤性、および耐低温性等を備えており、コンピュータ並びにIC制御の電気・電子機器部品材料として広く用いられている。

【0003】 近年、コンピュータ並びにIC制御の電気・電子機器の小型化・薄型化に伴い、配線基板類やICパッケージ材料も小型化・薄型化が求められるようになってきている。このため、これらに施される配線パターンも細密になり、フレキシブル配線板やTAB用キャリアテープ等に用いられるポリイミドフィルムについても加熱や引張り、さらには吸湿による寸法変化が小さいことが必要になる。さらに、材料の薄型化に伴い、積層体全体の「こし」を保ち、加工工程を安定にする必要もある。

【0004】 このような必要性を満たす為、ポリイミドフィルムは、線膨張係数が小さく、弾性率および貯蔵弾性率が高く、吸湿膨張係数が低いことが望まれる。

【0005】 ただし、フレキシブル配線板やICパッケージの製造の際、ポリイミドフィルムと銅箔とを張り合わせて加工するため、フィルム線膨張係数に関しては、銅の線膨張係数と大きく異なることは好ましくない。すなわち、ポリイミドフィルムと銅箔の線膨張係数が大きく異なると、張り合わせ品に反りが生じ、加工がしにくくなり、その結果、全体的な寸法精度や歩留まりが低下するからである。したがって、銅箔との線膨張係数の差が小さいものが好ましい。

【0006】 上記特性を有するポリイミドフィルムを得るため種々の試みがなされている。まず、ポリイミドフィルムの高弾性率化のためには、剛直な構造のモノマー即ち直線性の高いモノマーを用いれば良いことは広く知られている。ところが、直線性の高いモノマーを多量用いればフィルムの線膨張係数は低くなりすぎて、銅箔との張り合わせの用途には適さなくなる。

【0007】 比較的高い弾性率を実現しながらも線膨張係数を下げ過ぎないために、比較的剛直な構造を有するモノマーを用いて、化学的イミド化剤を用いず熱キュア法で製造し、面方向の配向を甘くするという方法を取る例もある。しかし、熱キュア法は化学的キュア法に比べ必要な加熱時間が長く、生産性に劣るという不利があ

る。

【0008】さらに、剛直で直線性の高いモノマーを用いると、一般的にはフィルムの柔軟性は損なわれ、フレキシブル配線板等としての利点の一つである折り曲げ可能という点に、難が生じる可能性がある。

【0009】半導体パッケージ用途等では、半導体の信頼性の観点から、特に吸水率ができるだけ低いことが求められ、寸法安定性の観点から、吸湿膨張係数も低いことが求められる。

【0010】吸水率や吸湿膨張係数を下げるには、分子構造中のイミド基量を減らすことが有効である。この為、屈曲基を主鎖中に複数含む長鎖のモノマーが使用されることが多い。しかし、この結果、弾性率の低下や線膨張係数の過度な増大を招き、寸法安定性が犠牲になる。極端な場合は、例えば200℃以下の低温にT_gを有するような熱可塑性を示すようになり、ベースフィルムとして用いるには適さなくなる。また、このような直線性で長いモノマーを用いると、分子鎖のパッキングが難しくなり、十分な靱性を発現することができず、場合によってはフィルム化すること自体が困難になる等の問題があった。

【0011】また、一般に粘弾性体（ポリイミドフィルムも含まれる）の貯蔵弾性率の値は、T_gを超える温度領域において、常温での貯蔵弾性率の値よりも低くなる（1桁、場合によっては2～3桁程度低くなる）ことが知られており、フィルム作製に通常使用する温度（例えば300℃以上400℃以下）における貯蔵弾性率が極端に小さい場合、フィルム作製の温度領域において極端にフィルムがたるむことなどにより、たるみの無い平坦なフィルムを作製すること自体が困難になる場合がある。

【0012】上述のように、ポリイミドフィルムの特性として要求される、高弾性率、高貯蔵弾性率、低線膨張係数、低吸水性の特性をすべて実現させるには、これらの特性以外にもフィルムの加工性等考慮すべき点が多く、いずれかの特性を満足させようとする、他の特性が犠牲になる等の問題があり、複数の良い特性をすべて併せ持つポリイミドフィルムを得ることは特に困難な状況であった。

【0013】

【発明が解決しようとする課題】そこで、本発明者らは、上記の問題点を解決し、高弾性率、高貯蔵弾性率、銅に近い線膨張係数、十分な靱性、低吸水性および低吸湿膨張係数の諸特性をすべて兼ね備える、細配線のフレキシブルプリント基板やTABフィルムに適したポリイミドフィルムを製造することに関し、鋭意検討を行った結果、本発明に到ったのである。

【0014】

【課題を解決するための手段】本発明者らは前述の要求に鑑み、特定の組成のポリイミドフィルムにおいて、特

異的に諸特性バランスを高度に実現し制御し得るポリイミドフィルム及びその製造方法を見出した。

【0015】本発明にかかるポリイミドフィルムの要旨とするところは、p-フェニレンビス（トリメリット酸モノエステル無水物）、オキシジフタル酸二無水物、（ピロメリット酸二無水物、3, 3', 4, 4'-ベンゾフェノンテトラカルボン酸二無水物、3, 3', 4, 4'-ビフェニルテトラカルボン酸二無水物からなる群から選択される1つ）、p-フェニレンジアミン、および4, 4'-ジアミノジフェニルエーテルとを有機溶剤中で反応させて得られるポリイミド酸から製造されることを内容とする。

【0016】前記ポリイミドフィルムにおいて、上記p-フェニレンビス（トリメリット酸モノエステル無水物）が、全酸二無水物に対して1～90モル%であり、オキシジフタル酸二無水物が、全酸二無水物に対して8モル%～85モル%であり、（ピロメリット酸二無水物、3, 3', 4, 4'-ベンゾフェノンテトラカルボン酸二無水物、3, 3', 4, 4'-ビフェニルテトラカルボン酸二無水物からなる群から選択される1つ）が、全酸二無水物に対して2～14モル%であり、p-フェニレンジアミンが、全ジアミンに対して25～90モル%であり、4, 4'-ジアミノジフェニルエーテルが、全ジアミンに対して10～75モル%であることを内容とする。

【0017】係るポリイミドフィルムにおいて、100℃から200℃の間の平均線膨張係数が15～30ppm、引張弾性率が4.5～8.5GPa、破断時伸び率が20%以上、吸湿膨張係数が10ppm以下、T_gが200℃以上、300℃以上400℃以下の温度における貯蔵弾性率が200MPa以上であることを内容とする。

【0018】本発明のポリイミドフィルムの製造方法の要旨とするところは、4, 4'-ジアミノジフェニルエーテルを有機溶剤中に溶解させ、（ピロメリット酸二無水物、3, 3', 4, 4'-ベンゾフェノンテトラカルボン酸二無水物、3, 3', 4, 4'-ビフェニルテトラカルボン酸二無水物からなる群から選択される1つ）を加え、続いてp-フェニレンジアミンを加え、該有機溶剤溶液にp-フェニレンビス（トリメリット酸モノエステル無水物）を加え、続いてオキシジフタル酸二無水物を加えて得られたポリイミド酸重合体を、脱水開環して、ポリイミドフィルムを得ることを内容とする。

【0019】本発明のポリイミドフィルムの製造方法の他の要旨とするところは、p-フェニレンジアミンを有機溶剤中に溶解させ、（ピロメリット酸二無水物、3, 3', 4, 4'-ベンゾフェノンテトラカルボン酸二無水物、3, 3', 4, 4'-ビフェニルテトラカルボン酸二無水物からなる群から選択される1つ）を加え、続いて、p-フェニレンビス（トリメリット酸モノエステ

ル無水物)を加え、該有機溶剤溶液に4, 4'-ジアミノジフェニルエーテルを加え、続いてオキシジフタル酸二無水物を加えて得られたポリアミド酸重合体を、酸無水物と第三級アミンとを用いて脱水閉環し、ポリイミドフィルムを得ることを内容とする。

【0020】

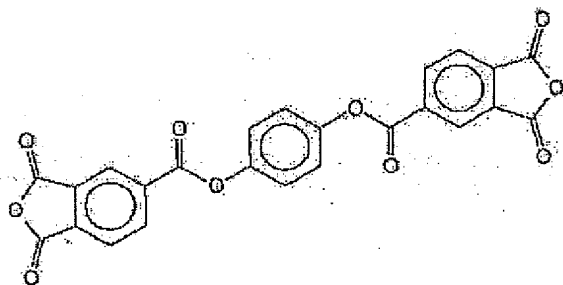
【発明の実施の形態】以下、本発明にかかるポリイミドフィルムについて、その実施の形態の一例に基づき説明する。なお、本発明の用語「モノマー」とは、単量体のジアミンあるいはテトラカルボン酸二無水物のいずれかをいう。

【0021】本発明にかかるポリイミドフィルムは、当業者に公知のポリアミド酸合成法により調製されたポリアミド酸から、製造され得る。好ましくは、本発明のポリイミドフィルムの製造方法では、上記脱水閉環が、酸無水物と第三級アミンとのイミド化剤の存在下で行われ得る。

【0022】本発明において、ポリアミド酸を合成する際には、酸二無水物として、特に、以下の構造式を持つp-フェニレンビス(トリメリット酸モノエステル無水物)(以下、TMHQという)

【0023】

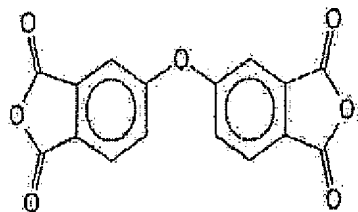
【化1】



【0024】および以下の構造式を持つオキシジフタル酸二無水物(以下、ODPAという)

【0025】

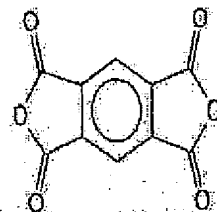
【化2】



【0026】および以下の構造式を持つピロメリット酸二無水物(以下、PMDAという)

【0027】

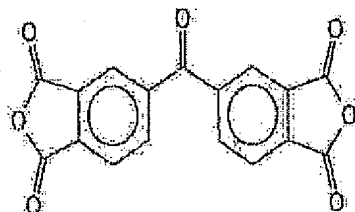
【化3】



【0028】および以下の構造式を持つ3,3',4,4'-ベンゾフェノンテトラカルボン酸二無水物(以下、BTDAという)

【0029】

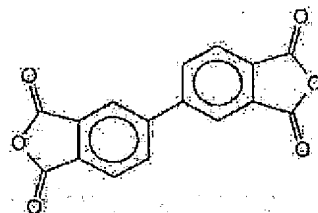
【化4】



【0030】および以下の構造式を持つ3,3',4,4'-ビフェニルテトラカルボン酸二無水物(以下、BPDAという)

【0031】

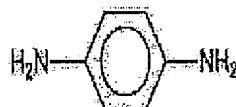
【化5】



【0032】ジアミンとして、以下の構造式を持つp-フェニレンジアミン(以下、PDAという)

【0033】

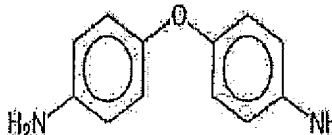
【化6】



【0034】および以下の構造式を持つ4,4'-ジアミノジフェニルエーテル(以下、ODAという)

【0035】

【化7】



【0036】を用いる。上記のモノマーを有機溶剤に溶解し、重合反応させて本発明にかかるポリイミドフィルムを製造するために用い得るポリアミド酸を得る。

【0037】以下TMHQは、PDAとの組み合わせにおいて、棒状構造をとり、フィルムの高弾性が顕現され、主鎖構造上エステル結合のため熱的にはやや柔軟であることから、例えばピロメリット酸のみを用いた場合

等に比べて線膨張係数が極端に下がることがなくなる。また、エステル結合がイミド環の分極を緩和し、吸水率を下げ吸水膨張率を下げる効果も有する。

【0038】ところが、TMHQは、PDAとの組み合わせでは、構造的に硬すぎ、線膨張係数も依然低く、また靱性が不十分である。ジアミノジフェニルエーテルを共重合することによっても、依然一定以上の弾性率を得ようとする線膨張係数は下がりすぎ、また靱性も不十分である。

【0039】ODPAを用いて、PDAとジアミノジフェニルエーテルとを重合させ、適度に高い弾性率と銅との組み合わせにおいて不都合のない適度な線膨張係数、また十分な靱性等を実現させ得る。ただし、ODPAだけでは吸水率そのものはさほど下ならず、吸湿特性を下げてかつ諸特性を好ましく保つにはTMHQをさらに共重合する、本発明の構成は、非常に有効である。

【0040】さらに、(PMDA、BTDA、BPDA)からなる群から選択される1つ)を共重合させることにより、ODPAおよびTMHQの組み合わせで実現できる好ましい他の特性を保持したまま、かつ、300°C以上400°C以下の温度における200MPa以上という高い貯蔵弾性率を新たに付与することができる、本発明の構成は、非常に有効である。

【0041】本発明の重合工程で用いられる有機溶剤は、当業者に公知の種々の溶剤を用い得る。例えば、ポリアミド酸に対して高い溶解性を有する高極性溶剤を用いることが好ましいが、これらの高極性溶剤に貧溶剤を添加することも可能である。高極性溶剤の例としては、N,N-ジメチルホルムアミド、N,N-ジメチルアセトアミド等のアミド類、N-メチル-2-ピロリドン等のピロリドン類、フェノール、p-クロロフェノール、o-クロロフェノール等のフェノール類等が挙げられる。貧溶剤の例としては、トルエン、テトラヒドロフラン、アセトン、メチルエチルケトン、メタノール、エタノール等が挙げられる。これらの溶剤を混合して、適度に溶解度パラメータを調整することにより、溶解性を高めることもできる。

【0042】上記酸二無水物及びジアミンの添加量は、上記p-フェニレンビス(トリメリット酸モノエステル無水物)が、全酸二無水物に対して0より多く90モル%以下の範囲、好ましくは1~90モル%であり、オキシジフタル酸二無水物が、全酸二無水物に対して9以上85モル%未満、好ましくは、8~85モル%であり、(ピロメリット酸二無水物、3,3',4,4'-ベンゾフェノンテトラカルボン酸二無水物、3,3',4,4'-ビフェニルテトラカルボン酸二無水物)からなる群から選択される1つ)が、全酸二無水物に対して1より多く15モル%以下の範囲、好ましくは2~14モル%であり、p-フェニレンジアミンが、全ジアミンに対して25~90モル%であり、4,4'-ジアミノジフェ

ニルエーテルが、全ジアミンに対して10~75モル%である。

【0043】ポリアミド酸の合成のための各モノマーの添加順序は特に限定されず、様々な方法が可能である。溶剤に、全ジアミンを溶解し、これにテトラカルボン酸二無水物を徐々に加えておおむね当量として粘度を調整しつつ、さらに残りのテトラカルボン酸二無水物をそのままあるいは適当な溶剤に溶解して加えて、当量比を等しくさせることが一般的に行われているが、これに限定されない。

【0044】これらの添加順序によっては、フィルムの特性を微妙に制御することも可能である。

【0045】具体的には、ODAとPDAを溶剤中に溶解し、これに対して、(PMDA、BTDA、BPDA)からなる群から選択される1つ)を加え、引き続きTMHQを加え、その後ODPAを加える方法；あるいは、同様に2種のジアミンを溶剤に溶解しておき、これに対して、(PMDA、BTDA、BPDA)からなる群から選択される1つ)を加え、引き続きこれにODPA、TMHQの順に酸二無水物を順次加える方法；または、同様に2種のジアミンを溶解しておき、これに3種の酸二無水物の混合物を加える方法；2種のジアミンのうちどちらか一方を溶剤に溶解しておき、これに3種の酸二無水物から選択される1種を加えて、その後もう1種のジアミンを加え、さらにその後もう2種の酸二無水物を加える方法、等を上げることができる。

【0046】1種のジアミンを複数のステップに分けて添加すると、さらにバリエーションは多くなり、これらにより種々の特性のさらなる微妙な調整が可能である。特にODAを有機溶剤中に溶解させ、これに、(PMDA、BTDA、BPDA)からなる群から選択される1つ)を加え、引き続きPDAを加え、これにTMHQを加え、続いてODPAを加えるという手順によって合成されたポリアミド酸を用いた場合は、上記のODAとPDAを入れ替えた順序を採用した場合よりも得られるポリイミドフィルムが高いT_gを示し、好ましい。

【0047】何れの場合もジアミン化合物のモル量の合計と酸二無水物化合物のモル量の合計は、ほぼ同一となるように用いる。

【0048】ここで、「ほぼ同一」としたのは、完全に同一であると重合度が過度に上がりすぎ、その結果溶液粘度が過度に上昇して取り扱いにくくなるからである。具体的には、ジアミン化合物モル量合計と、酸二無水物化合物モル量合計の比率は、0.95~1.05、好ましくは0.98~1.02の範囲であり、1:1でないことが特に好ましい。

【0049】それぞれのモノマーの添加割合は、特に限定されないが、好ましくは全酸二無水物中、TMHQは、0モル%より多く90モル%以下であり、ODPAは、9モル%以上85モル%未満であり、(PMDA、

BTDA、BPDAからなる群から選択される1つ)は、1モル%以上15モル%未満であり、全ジアミン中、PDAは、25モル%以上90モル%以下であり、ODAは、10モル%以上75モル%以下である。

【0050】特に好ましくは、全酸二無水物中、TMHQは、1モル%以上90モル%以下であり、ODPAは、8モル%以上85モル%以下であり、(PMDA、BTDA、BPDAからなる群から選択される1つ)は、2モル%以上14モル%以下である。

【0051】最も好ましくは、全酸二無水物中、TMHQは、5モル%以上50モル%以下であり、ODPAは、47モル%以上81モル%以下であり、(PMDA、BTDA、BPDAからなる群から選択される1つ)は、3モル%以上14モル%以下であり、全ジアミン中、PDAは、50モル%以上90モル%以下であり、ODAは、10モル%以上50モル%以下である。

【0052】これらの5種のモノマー以外のジアミンのモノマー成分を少量(ジアミン全体の10モル%以下の量)加え、得られるポリイミドフィルムの特性の微妙な調整をすることも可能である。使用するモノマーにもよるが、概ねこの量以下の共重合であれば、吸湿特性・熱特性・機械特性を好ましいレベルに保つことができる。少量用いるジアミンのモノマーとしては、ジメチルベンジジン、2, 2'-ビス(4-アミノフェノキシフェニル)プロパン、4, 4'-ビス(4-アミノフェノキシ)ビフェニル、またこれらのフッ素等ハロゲン置換体等を例示することができる。

【0053】重合反応は、一般的にポリアミド酸の重合反応に用いられる温度であれば、特に限定されないが、60℃以下が好ましく、40℃以下で行うことがより好ましい。高温度になると、酸無水物基の開環反応が生じ易く、ポリアミド酸の生成反応を阻害することがある。

【0054】重合反応は、窒素あるいはアルゴン等の不活性ガス中で行わせることが好ましいが、その他の条件下でも行い得る。

【0055】ポリアミド酸の溶液中の濃度は、5~30wt%、さらには10~25wt%が好ましい。これより低いと溶剤が増え、フィルム製造後の乾燥に時間がかかり、これより高い濃度の場合、粘度が上昇して加工が困難となる場合がある。

【0056】ポリアミド酸溶液の粘度は、フィルム加工できる粘度であれば特に限定されないが、22℃で約100~10000ポイズ程度、好ましくは、500~6000ポイズである。粘度が低過ぎるとフィルムの特性に悪影響を与え、加工の際に厚みを安定化することも難しい。一方、粘度が高過ぎる場合、溶液の攪拌が困難となり、フィルム状に加工する際に強い力が必要となり、不都合である。

【0057】得られたポリアミド酸の溶液を、フィルム状に形成し、ポリアミド酸をイミド化してポリイミドフ

ィルムを得ることができる。一般的には、このイミド化は、加熱により脱水する熱的方法および脱水剤あるいはイミド化触媒を用いる化学的方法とがある。このうちのいずれの方法を用いてもよく、化学的方法と熱的方法を併用することもできる。脱水剤と触媒を添加して加熱、乾燥する化学的方法によれば、熱的方法よりも効率がよく、優れた特性がフィルムに付与され得る。脱水剤あるいはイミド化触媒を用いない場合でも、本願発明の5種のモノマーを用いるならば製造工程で延伸工程を入れる等の方法により、同等の特性を実現することも可能であるが、生産性の面から、化学的方法が好ましい。

【0058】本発明に用いられる脱水剤は、例えば、無水酢酸等の脂肪族酸無水物、芳香族酸無水物などである。また、イミド化に用いられる触媒は、ピリジン、 α -ピコリン、 β -ピコリン、 γ -ピコリン、トリメチルアミン、ジメチルアニリン、トリエチルアミン、イソキノリンなどの第3級アミンなどである。

【0059】例えば、以下にイミド化の化学的方法の例を挙げるが、本発明はこれに限定されない。すなわち、得られたポリアミド酸溶液に化学量論以上の脱水剤と触媒量の第3級アミンとを加えた溶液を、支持板やPET等の有機化合物製のフィルム、ドラム、あるいはエンドレスベルト状に流延又は塗布して膜状とし、その膜を150℃以下の温度で約5分~90分間乾燥し、自己支持性のポリアミド酸重合体の塗膜を得る。次にこれを支持体より引き剥がして端部を固定する。その後、100℃~500℃程度まで徐々に加熱することによりイミド化させ、冷却後これより取り外してポリイミドフィルムを得る。

【0060】熱的方法によるイミド化の例は、上記の化学的イミド化法と同様の工程が挙げられるが、これに限定されない。すなわち、ポリアミド酸溶液を支持板やPET等の有機化合物製のフィルム、ドラムあるいはエンドレスベルト等の支持体上に流延または塗布して膜状とし、加熱処理し得る。

【0061】フィルムの製造に際しては、さらに、熱劣化防止剤を加えて焼成時のフィルムの劣化を防止し得る。その他の添加剤を加えて、フィルム製造時におけるフィルムの劣化等を防止することもできる。熱劣化防止剤としては、トリフェニルフォスフェイト等のリン酸系の劣化防止剤、置換基を有する又は置換基を有さないベンゾフェノン等が挙げられる。その他の添加剤としては、金属単体、有機金属化合物、またはガラス系のフィラー類等が挙げられる。

【0062】上記のようにして製造される本発明にかかるポリイミドフィルムは、一定の耐熱性、接着性等を有しつつ、高弾性率、高貯蔵弾性率、高破断伸び率、低線膨張係数、低吸湿膨張係数、それぞれの特性を有するバランスのよいポリイミドフィルムである。

【0063】具体的には、本発明にかかるポリイミドフ

フィルムは、100℃以上200℃以下の平均線膨張係数が15~30ppm、引張弾性率が4.5~8.5GPa、破断時伸び率が20%以上、吸湿膨張係数が10ppm以下、T_gが200℃以上、300℃以上400℃以下の温度における貯蔵弾性率が200MPa以上である特性を顕現することができる。

【0064】ここで、本発明にかかるポリイミドフィルムの特性は、以下のように測定したものである。すなわち、引張弾性率及び破断時伸び率とは、それぞれASTM-D882に準じた測定値をいう。平均線膨張係数は、セイコー電子工業株式会社製TMA120Cを用いて、窒素の存在下、1分間に10℃の割合で温度を上昇させて、100℃~200℃の時の値を測定して求める。吸湿膨張係数は、ポリイミドフィルムがたるまないように最低限の加重をかけた状態(5mm×20mmのサンプルに対して、約3g)で、湿度を30RH%に調湿し完全に飽和するまで吸湿させて寸法を計測し、その後湿度を90RH%に調湿し同様に飽和吸湿させた後寸法を計測し、両者の結果から相対湿度差1%あたりの寸法変化率を求める。ガラス転移温度(T_g)は、動的粘弾性測定装置(セイコー電子工業株式会社製DMS200)を用いて引張モードで、3℃/分の割合で昇温させながら測定する。

【0065】

【実施例】以下に実施例により本発明をより具体的に説明するが、本発明はこれら実施例によって限定されるものではない。

【0066】(実施例1)窒素置換雰囲気中の氷浴下でジメチルアセトアミド780g中に、33.4g(総ジアミン中の約37.5mol%)のODAを溶解し、3.9g(総酸二無水物中の約4mol%)のPMDAを溶解し、30.0g(総ジアミン中の約62.5mol%)のPDAを溶解し、これにTMHQ63.1g(総酸二無水物中の約31mol%)を徐々に加えて良く攪拌し反応させ、続いてODPA89.6g(総酸二無水物中の約65mol%)を徐々に加え、23℃での測定で約2500ポイズのポリイミド酸溶液を得た。

【0067】このポリイミド酸溶液100gを0℃程度に冷却し、これに13.5gの無水酢酸と4.1gのイソキノリンを加えて、均一に攪拌しこれを、SUS板上に焼成後50μmになるような所定の厚みにキャストし、125℃で5分熱風乾燥した。その後SUS板よりフィルムを引き剥がし、これを4片を固定した状態で170℃で1.5分、250℃で1.5分、350℃で3分、430℃で3分加熱乾燥し、ポリイミドフィルムを得た。このフィルムの引張弾性率、破断時伸び率、線膨張係数、吸湿膨張係数、T_g、350℃での貯蔵弾性率を測定した結果を表1に示す。

【0068】(実施例2)窒素置換雰囲気中の氷浴下でジメチルアセトアミド780g中に、33.6g(総ジ

アミン中の約37.5mol%)のODAを溶解し、7.8g(総酸二無水物中の約8mol%)のPMDAを溶解し、30.3g(総ジアミン中の約62.5mol%)のPDAを溶解し、これにTMHQ63.6g(総酸二無水物中の約31mol%)を徐々に加えて良く攪拌し反応させ、続いてODPA84.7g(総酸二無水物中の約61mol%)を徐々に加え、23℃での測定で約2500ポイズのポリイミド酸溶液を得た。

【0069】このポリイミド酸溶液を実施例1と同様の方法で加工し、ポリイミドフィルムとした。実施例1と同様に、特性試験を行った。その結果を表1に示す。

【0070】(実施例3)窒素置換雰囲気中の氷浴下でジメチルアセトアミド780g中に、33.9g(総ジアミン中の約37.5mol%)のODAを溶解し、11.8g(総酸二無水物中の約12mol%)のPMDAを溶解し、30.5g(総ジアミン中の約62.5mol%)のPDAを溶解し、これにTMHQ64.1g(総酸二無水物中の約31mol%)を徐々に加えて良く攪拌し反応させ、続いてODPA79.8g(総酸二無水物中の約57mol%)を徐々に加え、23℃での測定で約2500ポイズのポリイミド酸溶液を得た。

【0071】このポリイミド酸溶液を実施例1と同様の方法で加工し、ポリイミドフィルムとした。実施例1と同様に、特性試験を行った。その結果を表1に示す。

【0072】(実施例4)窒素置換雰囲気中の氷浴下でジメチルアセトアミド780g中に、33.1g(総ジアミン中の約37.5mol%)のODAを溶解し、7.1g(総酸二無水物中の約5mol%)のBTDAを溶解し、29.8g(総ジアミン中の約62.5mol%)のPDAを溶解し、これにTMHQ62.6g(総酸二無水物中の約31mol%)を徐々に加えて良く攪拌し反応させ、続いてODPA87.5g(総酸二無水物中の約64mol%)を徐々に加え、23℃での測定で約2500ポイズのポリイミド酸溶液を得た。

【0073】このポリイミド酸溶液を実施例1と同様の方法で加工し、ポリイミドフィルムとした。実施例1と同様に、特性試験を行った。その結果を表1に示す。

【0074】(実施例5)窒素置換雰囲気中の氷浴下でジメチルアセトアミド780g中に、33.0g(総ジアミン中の約37.5mol%)のODAを溶解し、17.7g(総酸二無水物中の約12.5mol%)のBTDAを溶解し、29.7g(総ジアミン中の約62.5mol%)のPDAを溶解し、これにTMHQ62.5g(総酸二無水物中の約31mol%)を徐々に加えて良く攪拌し反応させ、続いてODPA77.1g(総酸二無水物中の約56.5mol%)を徐々に加え、23℃での測定で約2500ポイズのポリイミド酸溶液を得た。

【0075】このポリイミド酸溶液を実施例1と同様の方法で加工し、ポリイミドフィルムとした。実施例1と

同様に、特性試験を行った。その結果を表1に示す。

【0076】（実施例6）ODAとPDAの添加順序を逆にした以外はすべて実施例5と同様の方法で重合を行い、同様の方法でポリイミドフィルムを作製し、特性試

験を行った。その結果を表1に示す。

【0077】

【表1】

	構成成分 (モル%)	引張弾性率 (GPa)	伸び率 (%)	熱膨張 係数 (ppm)	変形 係数 (ppm)	ガラス 転移温度 (°C)	350°Cでの 貯蔵弾性率 (MPa)
実施例1	ODA 37.5	6	30	21	8	240	210
	PMDA 4						
	PDA 62.5						
	TMHQ 31						
	ODPA 65						
実施例2	ODA 37.5	6	28	21	7	250	240
	PMDA 8						
	PDA 62.5						
	TMHQ 31						
	ODPA 61						
実施例3	ODA 37.5	6	30	20	7	255	270
	PMDA 12						
	PDA 62.5						
	TMHQ 31						
	ODPA 57						
実施例4	ODA 37.5	6	30	21	6	250	260
	BTDA 5						
	PDA 62.5						
	TMHQ 31						
	ODPA 64						
実施例5	ODA 37.5	6	28	21	7	260	310
	BTDA 12.5						
	PDA 62.5						
	TMHQ 31						
	ODPA 56.5						
実施例6	PDA 62.5	6	25	19	7	250	350
	BTDA 12.5						
	ODA 37.5						
	TMHQ 31						
	ODPA 56.5						
実施例7	PDA 62.5	6	25	21	7	275	360
	BTDA 12.5						
	TMHQ 31						
	ODA 37.5						
	ODPA 56.5						

【0078】（実施例7）窒素置換雰囲気中の氷浴下でジメチルアセトアミド780g中に、29.7g（総ジアミン中の約62.5mol%）のPDAを溶解し、17.7g（総酸二無水物中の約12.5mol%）のBTDAを溶解し、これにTMHQ62.5g（総酸二無水物中の約31mol%）を徐々に加えてよく攪拌反応させ、33.0g（総ジアミン中の約37.5mol%）のODAを溶解し、続いてODPA77.1g（総酸二無水物中の約56.5mol%）を徐々に加え、23°Cでの測定で約2500ポイズのポリアミド酸溶液を得た。このポリアミド酸溶液を実施例1と同様の方法で加工し、ポリイミドフィルムとした。実施例1と同様

に、特性試験を行った。その結果を表1に示す。

【0079】（比較例1～4）実施例と同様の方法で、ジメチルアセトアミド中にジアミン成分を全て溶解した後酸二無水物を加える方法で、溶液中の総固形分濃度20%、および粘度2500ポイズになるように重合反応をおこなった。各成分とそのモル%は表2に示している。実施例と同様にこれらのポリアミド酸溶液を用いてポリイミドフィルムを得て、その特性を測定した結果を表2に示す。

【0080】

【表2】

	構成成分 (モル%)	引張弾性率 (GPa)	破断時 伸び率 (%)	線膨張 係数 (ppm)	吸湿 膨張係数 (ppm)	ガラス 転移温度 (°C)	350°Cでの 貯蔵弾性率 (MPa)
比較例1	ODA 40 PDA 60 TMHQ 100	8.5	5	18	6	270	1000
比較例2	ODA 37.5 PDA 62.5 TMHQ 31 ODPA 69	6	30	23	5	255	150
比較例3	ODA 50 PDA 50 TMHQ 50 PMDA 50	5.5	20	9	6	350	1100

【0081】

【発明の効果】本発明のポリイミドフィルムはこれまでのベース用ポリイミドフィルムに無い優れた吸湿特性、特に低い吸湿膨張を有し、なおかつ高弾性、高貯蔵弾性率でありながら銅の線膨張係数を下回ることなく、従っ

て銅張の基板やTAB用テープとして用いた場合に極めて優れた反り特性を発現できる。本発明のポリイミドフィルムは、柔軟性・耐熱性にも優れ、ベースポリイミドフィルムとして必要な特性を損なわないため、益々細密化する電子機器に対応することができる。

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